WATER WATER WATER WATER WATER WATER WATER WATER WATER WATER WATER

FILE

PROJECT COMPLETION
REPORT NO. 347X

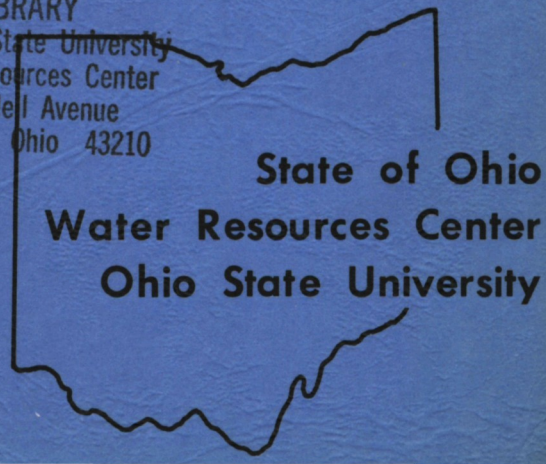
Precipitation of Phosphates from Water with Ferrous Salts

By
Karlis Svanks

1971

United States Department of the Interior

CONTRACT NO.
A-011-Ohio
AA14-01-0001-1855



State of Ohio
Water Resources Center
Ohio State University

PRECIPITATION OF PHOSPHATES FROM WATER WITH FERROUS SALTS

by

Karlis Svanks
Assistant Professor
Chemical Engineering Department
The Ohio State University, Columbus

WATER RESOURCES CENTER
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO 43210

February, 1971

This study was supported in part by
the Office of Water Resources
Research, U. S. Department of Interior
under Project A-011-OHIO

ABSTRACT

of

PRECIPITATION OF PHOSPHATES FROM WATER
WITH FERROUS SALTS

The use of ferrous sulfate for precipitating phosphate from water was investigated. Different phosphate containing solutions were evaluated: (1) pure orthophosphate, (2) secondary effluent from a waste treatment plant, and (3) precipitation of phosphate in a simulated activated sludge process.

Studies were made to determine the effect of dissolved oxygen concentration, pH, and iron-to-phosphate ratio on the removal of phosphate. In addition, the relative effectiveness of calcium hydroxide and sodium hydroxide for control of pH and the use of microflotation and dissolved air flotation for separation of the phosphate precipitate were evaluated.

In all cases, maximum phosphate removal (up to 97 percent) was obtained when the pH was 7 to 8, the molar iron to phosphate ratio greater than 1.5 and dissolved oxygen concentration equal to that required for complete oxidation of ferrous iron.

Calcium hydroxide was found to be a more effective base since the optimal pH range was expanded and the coagulation and flocculation of the insolubilized phosphates were improved.

Interferences from organic matter in secondary effluents on flotation operations were observed.

Ferrous sulfate should be very effective for removing phosphate in the activated sludge process. The low dissolved oxygen concentration will control the oxidation of ferrous iron to optimal rates, and the sludge will increase the settling rate of the phosphate precipitate.

Key words: Phosphate removal, Ferrous sulfate, Phosphate, Dissolved oxygen, Precipitation, Sedimentation, Flotation, Secondary effluent, Wastewater, Sewage, Activated sludge process.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (Con't.)

LIST OF FIGURES (Con't.)

LIST OF FIGURES (Con't.)

LIST OF TABLES

SECTION 1.

CONCLUSIONS AND RECOMMENDATIONS

The following major conclusions appear to be supported by the results obtained during the course of this study:

(1) Phosphate is precipitated from pure oxygen-free solutions of phosphate by ferrous sulfate as ferrous phosphate having a mole ratio of iron to phosphorus of 1.5. Using calcium hydroxide for pH adjustment the optimal pH range is expanded and the coagulation and flocculation properties of the insolubilized compounds is improved. The residual concentration of iron decreases with increasing pH.

(2) Higher phosphate removal by ferrous sulfate is achieved from oxygen-containing pure phosphate solutions compared to phosphate removal from oxygen-free solutions. Relatively higher phosphate removal is attained when oxygen is present in a quantity theoretically required for complete oxygenation of ferrous iron. Phosphate removal decreases rapidly when mole ratio of iron to phosphorus decreases below 1.5

(3) The removal of insolubilized phosphates by dissolved air flotation is more efficient than microflotation when pure phosphate solutions are used.

(4) The removal of phosphates from secondary effluent is similar to phosphate removal from oxygen-containing pure phosphate solutions at similar conditions. The phosphate removal is not affected by contaminants commonly occurring in secondary effluent.

(5) The organic matter present in secondary effluent affects the removal of insolubilized phosphates with ferrous sulfate by dissolved air flotation technique through a lowering of the froth stability.

(6) The removal of phosphates with ferrous sulfate in an activated sludge process is attractive considering the efficiency of phosphate removal, residual iron concentration and economics of the process. The optimal condition at which phosphates are efficiently removed from pure oxygen-containing solutions are closely approached in an activated sludge process.

Recommendations

(1) The separation of insolubilized phosphates by dissolved air flotation technique has many attractive aspects, but to evaluate the feasibility of the process, more laboratory work is required.

(2) In view of the excellent results obtained from laboratory-scale investigations of phosphate removal by ferrous sulfate in an activated sludge process, we recommend that small plant scale studies be made in order to evaluate the economics of the process and to develop engineering data required for design of equipment and procedures that could be used in large capacity sewage treatment plants.

SECTION 2.

INTRODUCTION

It is generally agreed that the eutrophication of lakes and streams is caused mainly by fertilizing elements such as phosphates and nitrogen. Domestic wastewaters have been indicated as major sources of phosphates and nitrogen compounds. Conventional treatment methods for municipal wastewaters were not designed to remove these nutrients effectively. Since phosphorus is considered the key element in fertilization of natural bodies of water (1), the importance of its removal from recycled water is self evident.

During the past two decades extensive work was done on phosphate removal from wastewater. The conversion of soluble phosphates to an insoluble form by mineral addition and the separation of insolubilized phosphates by sedimentation was found to be economically and technologically feasible.

Calcium hydroxide, aluminum sulfate, sodium aluminate and ferric salts were found effective in phosphate removal.

The removal of phosphates from water with ferrous salts appeared attractive based on the following considerations:

(1) Ferrous sulfate is the cheapest reagent when compared to alum, sodium aluminate, ferric chloride and ferric sulfate.

(2) Ferrous hydroxide has the highest solubility in water at a pH of approximately 7 when compared to ferric hydroxide and aluminum hydroxide. Therefore the equilibrium should be shifted toward ferrous phosphate formation and consequently should improve the phosphate removal in oxygen-free aqueous solutions.

(3) By precipitation of phosphate with ferric salts at a pH close to 7 at least two reactions proceed simultaneously: (1) the formation and precipitation of ferric hydroxide and (2) formation and precipitation of ferric phosphates. Phosphate removal is therefore the result of the kinetics of the two reactions which in turn are pH dependent. When using ferrous salts in oxygen-containing solutions, at least the following reactions proceed simultaneously: the oxidation of ferrous ions to ferric ions; the hydrolysis of ferric ions by formation and precipitation of ferric hydroxide; the reaction of ferrous or ferric ions with phosphate to form ferric phosphate or ferrous phosphate which subsequently will be oxidized to ferric phosphate.

It was assumed that the rate of formation of the ferric hydroxide precipitate will be slower when using ferrous ions than in the case where ferric ions are added directly. Consequently, the efficiency of phosphate removal will be improved.

The separation of formed solids by flotation techniques appeared attractive because this type of separation may be accomplished in a short period of time and the required volume of flotation tanks is much smaller than in the case of sedimentation tanks. The laboratory work on

flotation processes reported below were made to determine the feasibility of such processes in wastewater treatment.

OBJECTIVES

The main objectives of this work were to determine:

(1) The mechanism of the reaction and conditions under which ferrous sulfate may be used to remove phosphates from water.

(2) Methods of removing the insoluble phosphates formed in the reaction, with particular emphasis on flotation processes.

(3) The removal of phosphates with ferrous sulfate from sewage treatment plant secondary effluent and the effect on COD.

(4) The removal of phosphates with ferrous sulfate concurrently with simulated activated sludge process.

SECTION 3

RELATED LITERATURE

W. L. Lea, et.al. (2) reported that phosphates are effectively removed with ferrous sulfate. These authors also stated that the phosphate was removed with alum and ferric sulfate by adsorption on hydroxide flocs, but that phosphates can be removed with ferrous sulfate by a chemical reaction which may occur during the transition from ferrous to ferric hydroxide.

I. Rippert (3) showed that phosphate may be removed effectively with ferrous sulfate from air-free solutions and that the oxidation of ferrous to ferric hydroxide is not necessary to attain efficient phosphate removal. Rippert used such a large excess of ferrous sulfate (mole ratio of Fe:P from 8 to 4) to attain efficient phosphate removal that the process would not be economical. Rippert also did some work on poly-phosphate removal with ferrous and ferric sulfates which showed that poly-phosphates are removed with ferrous and ferric sulfates but less efficiently than ortho-phosphates.

Contrarily, A. Henriksen (4) states that poly-phosphates are removed more efficiently than ortho-phosphates with ferric sulfate.

Ronald F. Wukasch (5) reported that phosphates are efficiently removed with ferrous chloride by addition of a strong base and a flocculation agent (Purifloc A-23, a high molecular weight anionic polyelectrolyte manufactured by Dow Chemical company). He also stated that the transient strong base alkalinity modified the colloidal properties of the system before the flocculation agent became effective and that phosphate insolubilization is not a pH associated phenomenon. Wukasch also found vivianite ($Fe_3(PO_4)_2 \cdot 8\ H_2O$) in the sludge, by x-ray diffraction analysis. The phosphates were removed from raw sewage in primary sedimentation tanks. The oxygen concentration in the raw sewage was not reported, but it may be assumed to be very low.

G. Schuster (6) reported in 1968 that phosphates are efficiently removed with ferrous sulfate at pH = 7.5 when the pH is adjusted using HCl or NaOH. Ortho-phosphate is removed more efficiently than poly-phosphates.

G. Rudolf and D. Uhlmann (7) reported in 1968 that phosphates are efficiently removed from sewage at pH = 7.0 to 7.3 with ferrous sulfate when oxygen is present to oxidize the ferrous to ferric iron.

Van Vuuren, et.al. (8) has combined the chemical precipitation of phosphate by lime with a foam separation technique.

SECTION 4

PRELIMINARY RUNS

The purpose of this preliminary work was:

(1) To compare phosphate removals by ferrous sulfate, ferric chloride, and alum at similar conditions, and

(2) To evaluate which variables are most important in determining the efficiency of phosphate removal with ferrous sulfate.

In Tables I, II, and III are listed some results of the preliminary work done by Chun-jen Wang (9). All solutions contained dissolved oxygen in equilibrium with air. The precipitation of phosphates was performed in 1000 ml beakers with 800 ml pure phosphate solutions (KH_2PO_4). The solution was stirred on a Phipps and Bird variable speed multiple stirrer (1" x 3" blades) at 100 RPM while reagents were added (solid $FeSO_4 \cdot 7\ H_2O$, $FeCl_3 \cdot 6\ H_2O$ and $Al_2(SO_4)_2 \cdot 18\ H_2O$ as solution) and the pH was adjusted with NaOH solution or $Ca(OH)_2$ - suspension. Solutions were added and the pH adjusted within approximately 5 minutes.

The suspension was stirred for 10 minutes at 20 RPM and allowed to settle under quiescent conditions.

Table I shows that all three metals salts were very efficient reagents for phosphate removal in the pH range from 7.0 to 7.5 when $Ca(OH)_2$ was used to adjust the pH. Table I also shows that the mole ratio of metal to phosphorus and the settling time have a pronounced effect on phosphate removal for the same initial concentration of phosphate solution.

Table II shows that $Ca(OH)_2$ is superior to NaOH as a pH adjustment reagent. It was observed that $Ca(OH)_2$ was superior to NaOH as a coagulation and flocculation reagent because higher settling rates were attained. The effect was most pronounced when ferrous sulfate was used for phosphate removal.

Table III shows the comparison of $Ca(OH)_2$ and NaOH as pH adjusting reagents when ferrous sulfate was used for phosphate removal. Phosphate removal decreased rapidly with increasing pH when NaOH was used. This was attributed to the reaction

$$FePO_{4(s)} + 3\ OH^- \longrightarrow Fe(OH)_{3(s)} + PO_4^{-3}$$

In the presence of calcium ions, insoluble calcium phosphate is formed and only a slight decrease of phosphate removal was observed.

TABLE I. PHOSPHATE REMOVAL BY ALUM, FERRIC CHLORIDE AND FERROUS SULFATE
ORIGINAL PHOSPHATE SOLUTION: 35.0 mg/l PO_4 ADDED AS KH_2PO_4.
pH ADJUSTED WITH APPROXIMATELY 0.2 NORMAL $Ca(OH)_2$-SUSPENSION.

Reagent mg/l	Mole ratio of metal to P	pH	Settling time hours	PO_4 mg/l in supernatant	% PO_4 removed	Settling time hours	PO_4 mg/l in supernatant	% PO_4 removed
$Al_2(SO_4)_2 \cdot 18\ H_2O$	Al:P							
390	3.2	7.3	1	0.39	98.9	24	0.15	99.6
300	2.4	7.0	1	0.91	97.4	24	0.58	98.3
250	2.0	7.2	1	1.83	94.8	24	2.60	92.6
$FeCl_3 \cdot 6\ H_2O$	Fe:P							
300	3.0	7.1	1	0.25	99.3	24	0.08	99.8
200	2.0	7.5	1	0.37	98.7	24	0.36	99.0
150	1.5	7.1	1	0.82	97.7	24	0.78	97.8
$FeSO_4 \cdot 7\ H_2O$	Fe:P							
400	3.9	7.4	1	0.24	99.3	24	0.0	100
300	2.9	7.3	1	1.2	96.6	24	0.55	98.4
150	1.5	7.3	1	3.0	91.4	24	0.90	97.4

TABLE II. COMPARISON OF NaOH AND $Ca(OH)_2$ AS pH ADJUSTING REAGENTS ORIGINAL PHOSPHATE SOLUTION: 35.0 mg/l PO_4 ADDED AS KH_2PO_4

Reagent	mg/l	Mole ratio of metal to P	pH	Settling time	pH adjusting reagent	PO_4 mg/l left in solution	% P removed
$FeSO_4 \cdot 7 H_2O$	306	3.0	7.3	20 min	0.1 N $Ca(OH)_2$	0.48	98.6
$FeSO_4 \cdot 7 H_2O$	306	3.0	7.3	20 min	0.1 N NaOH	6.12	82.5
$FeCl_3 \cdot 6 H_2O$	295	3.0	7.1	1 hour	0.1 N $Ca(OH)_2$	0.78	97.8
$FeCl_3 \cdot 6 H_2O$	295	3.0	8.2	1 hour	0.1 N NaOH	Colloidal	Suspension
$Al_2(SO_4)_3 \cdot 18 H_2O$	390	3.0	7.0	1 hour	0.1 N $Ca(OH)_2$	1.56	95.5
$Al_2(SO_4)_3 \cdot 18 H_2O$	390	3.0	7.3	1 hour	0.1 N NaOH	1.20	96.6

TABLE III. COMPARISON OF NaOH AND $Ca(OH)_2$ AS pH ADJUSTING REAGENTS PHOSPHATE REMOVAL WITH FERROUS SULFATE.[2] PO_4 ADDED AS KH_2PO_4, APPROXIMATELY 0.1 NORMAL $Ca(OH)_2$-SUSPENSION, 0.1 NORMAL NaOH SOLUTION. SETTLING TIME 24 HOURS.

PO_4 mg/l	$FeSO_4 \cdot 7\ H_2O$ mg/l	Mole ratio Fe:P	NaOH			$Ca(OH)_2$		
			pH	PO_4 left mg/l	% PO_4 removed	pH	PO_4 left mg/l	% PO_4 removed
7.0	150	7.34	6.9	0.15	97.9	6.5	0.0	100
7.0	150	7.34	8.5	5.6	7.2	8.8	0.13	98.2
7.0	150	7.34	9.7	high	--	9.4	0.15	97.8
18.0	300	5.6	6.8	0.38	97.9	6.8	0.2	99.5
18.0	300	5.7	8.0	0.94	94.6	7.8	0.0	100
18.0	300	5.7	9.2	1.84	89.4	8.9	0.4	97.8
35.0	460	4.5	7.2	0.0	99.5	7.0	0.0	100
35.0	460	4.5	8.0	1.43	95.9	8.0	0.0	100
35.0	460	4.5	9.1	8.9	74.6	9.5	0.5	98.7
70.0	610	3.0	7.5	0.0	100	7.2	0.05	99.9
70.0	610	3.0	8.1	1.27	98.2	8.0	0.09	99.8
70.0	610	3.0	9.0	high	--	9.1	0.50	99.3

$Ca(OH)_2$ was found superior to NaOH in many respects:

(1) $Ca(OH)_2$ (lime) is less expensive than NaOH.

(2) The coagulation and flocculation rates of the iron phosphates and iron hydroxides and consequently their settling rates were increased by the presence of calcium ions.

(3) Phosphate removal with ferrous sulfate was improved when $Ca(OH)_2$ was used for pH adjustment.

(4) Phosphate removal decreased only slightly when pH = 7 was exceeded when adjusting the solutions with $Ca(OH)_2$.

The negative side effect of $Ca(OH)_2$ used for pH adjustment was due to the increase of calcium ions (hardness) in the treated water.

It was observed that dissolved oxygen had a pronounced effect on the color of the precipitates formed, indicating that ferrous iron was being oxidized. The oxidation of ferrous iron proceeds according the reaction:

$$Fe^{+2} + 1/4\ O_2 + H^+ \rightarrow Fe^{+3} + 1/2\ H_2O$$

The preliminary runs were performed over a pH range of approximately 6.5 to 9.5. In this range of pH the ferric iron is rapidly hydrolyzed according to the reaction:

$$Fe^{+3} + 3\ H_2O \rightarrow Fe(OH)_{3(s)} + 3\ H^+$$

The overall reaction may be written:

$$Fe^{+2} + 1/4\ O_2 + 2\text{-}1/2\ H_2O \rightarrow Fe(OH)_{3(s)} + 2\ H^+$$

The formation of $FePO_4$ proceeds simultaneously with the hydrolysis of ferric iron. The extent of phosphate removal is then the net result of the two competing reactions and is associated with a decrease of pH. The decrease of pH with time was observed experimentally.

According to the oxidation reaction of ferrous iron, 8 mg of O_2 can oxidize at the most 55.84 mg iron. The preliminary runs showed that the precipitates formed had a reddish-brown color when iron concentration in the solutions was below approximately 56 mg/l. The oxygen concentration was approximately 8 mg/l at the experimental conditions. This implies that most of the ferrous iron was oxidized to ferric iron. When the concentration of iron in the solutions was above 56 mg, the precipitate color became dark blue and the oxygen concentration in solution rapidly decreased to near zero. This indicated the formation of ferro-ferric compounds.

From the above discussion it is evident that the extent of phosphate removal with ferrous sulfate in the presence of oxygen is also affected by the oxidation rate of ferrous iron which is pH dependent.

This preliminary work showed that ferrous sulfate was an excellent reagent for phosphate removal from water. The main variables affecting the efficiency of phosphate removal were pH, pH adjusting reagents, oxygen concentration, mole ratio of Fe to P, and settling time. The following experimental program was developed to study these variables and their effect on the removal of phosphate.

SECTION 5

PRECIPITATION OF PHOSPHATE FROM OXYGEN - FREE PURE PHOSPHATE SOLUTIONS WITH FERROUS SULFATE AND SEPARATION OF THE PRECIPITATE BY SEDIMENTATION

Exclusion of oxygen from solutions eliminated one of the variables of the system under study: the oxidation of ferrous iron. This relatively simple process, compared to systems containing dissolved oxygen, was investigated for effects of: (1) pH; (2) NaOH and $Ca(OH)_2$ as pH-adjusting reagents; (3) the mole ratio of Fe to P; and, (4) settling time of the precipitate on phosphate removal from the solution.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

The precipitation and sedimentation cell, shown in Figure 1, consisted of a one-quart battery jar sealed with a Neoprene cover plate. In the cover plate were mounted: (1) oxygen probe connected to a Yellow Spring Instrument Co. Model 51 oxygen meter; (2) pH-combination electrode (Sargent S-30072-15) connected to Sargent Model LS pH-meter; (3) nitrogen inlet tube (fritted glass cylinder type, coarse); and (4) stainless steel stirrer (paddle, 1" by 3") driven by a variable speed motor. A port was also provided for addition of the reagents. Phosphate solution (KH_2PO_4) was added to the jar and nitrogen was bubbled through the solution until the oxygen concentration was essentially zero. Approximately 20 minutes were required to reach zero oxygen.

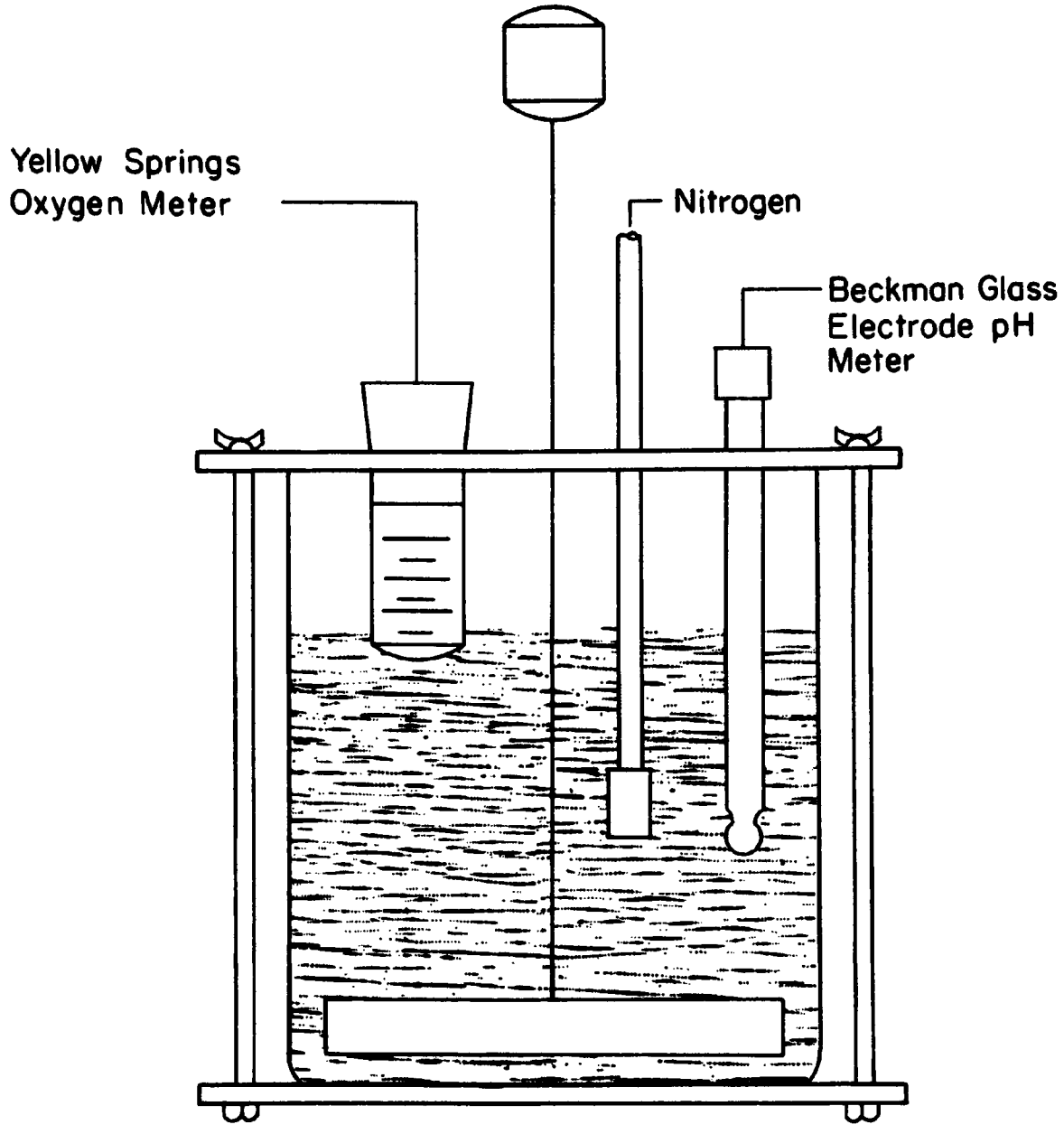


Figure 1. Sedimentation cell for ferrous iron-orthophosphate precipitation.

The nitrogen inlet tube was then pulled above the solution level and a lively stream of nitrogen was added to prevent entrance of oxygen from the air. Weighed quantities of solid $FeSO_4 \cdot 7\ H_2O$ were added to the solution through the port and dissolved by stirring. The pH was then adjusted with oxygen-free NaOH solution or $Ca(OH)_2$ suspension by stirring at 100 R.P.M. The suspension was stirred for 5 to 20 minutes at 20 R.P.M. to aid flocculation and then left to settle under quiescent conditions. Supernatant samples were withdrawn after settling times varying from 20 minutes to 22 hours, and analyzed for phosphate, iron, and calcium.

Analytical Procedures

I. Determination of Calcium.

Calcium was determined with Perkin-Elmer 303 atmoic absorption spectrophotometer.

The determination of the phosphate was made by the Molybdemum Blue-Hydrizine Sulfate Photometric Method adapted for water analysis from the 1964 Book of A.S.T.M. Standards, Part 32, Chemical Analysis of Metals, pp. 97-100. This analysis method offers the lease interference from iron.

Analysis for iron was made using the Phenanthroline Photometric Method adapted for water analysis from Standard Methods, Twelfth Edition (1965), prepared and published by the American Health Association.

II. Determination of Phosphorus in Water by the Molybdenum Blue Photometric Method.

Reagents

(a) Ammonium Molybdate Solution (20 g. per liter). Add 300 ml H_2SO_4 to 500 ml of water and cool. Add 20 g. of ammonium heptamolybdate ($(NH_4)_6MO_7O_{24}\cdot 4H_2O$) and dilute to 1 liter.

(b) Hydrazine Sulfate Solution (1.5 g. per liter). Dissolve 1.5 g. of hydrazine sulfate ($(NH_2)_2\cdot H_2SO_4$) in water and dilute to 1 liter.

(c) Ammonium Molybdate-Hydrazine Sulfate Solution. Dilute 250 ml of the ammonium molybdate solution to 600 ml, add 100 ml of the ($(NH_2)_2 \cdot H_2SO_4$) solution, and dilute to 1 liter. Prepare immediately before use.

(d) Phospharus Standard Solution. (1 ml = 0.05 mg. P). Dissolve 0.2292 g of sodium manohydrogen phosphate (Na_2HPO_4) in about 200 ml of water. Add 100 ml of $HClO_4$(1:5) and dilute to 1 liter in a volumetric flask.

(e) Sodium Sulfite Solution. (100 g per liter). Dissolve 100 g of sodium sulfite (Na_2SO_3) in water and dilute to 1 liter. Prepare as needed.

Preparation of Calibration Curve

Transfer 10 ml of the standard phosphorus solution (1 ml = 0.05 mg P) to a 100 ml volumetric flask; add 1 ml $HClO_4$ and dilute to the mark. Use seven 100 ml volumetric flasks. Transfer to flasks No. 2,3, 4, 5, 6, and 7 - 1, 2, 4, 6, 8, and 10 ml of the diluted phosphorous standard solution (1 ml = 0.005 mg P) respectively and dilute to 25 ml with water. To flask 1 add only 25 ml of distilled water. Add 1 ml of $HClO_4$ and 15 ml of Na_2SO_3 solution to each flask. Boil gently for 30 seconds, and immediately add 50 ml of the freshly prepared ammonium molybdate-hydrazin e sulfate solution. Heat on a steam bath at 85 to 90° for 20 min. and then quickly cool to 20° C. Dilute to the mark and mix. (The color is stable for approximately 2 hours).

Photometry

Transfer a portion of the reference (blank, flask 1) solution to an adsorption cell and adjust the photometer to the initial setting using a light band centered at approximately 830 mu. While maintaining the photometric readings of the calibration solutions.

Calibration Curve

Plot the photometric readings of the calibration solutions against milligrams of phosphorus per 100 ml of solution.

Procedure

Transfer 25 ml of water sample or smaller sample diluted with water to 25 ml to a 100 ml volumetric flask (25 ml of distilled water as blank solution). Add to each flask 1 ml $HClO_4$ and 15 ml of Na_2SO_3 solution. Boil gently for 30 seconds, and immediately add 50 ml of the freshly prepared ammonium molybdate-hydrazine solution. Heat on a steam bath at 85-90° C for 20 minutes and then quickly cool to 20° C. Dilute to mark and mix. Proceed as directed in preparation of calibration curve under photometry using blank solution as reference. Read from plot the P content.

III. Determination of Iron in Water by the Phenanthroline Method

Reagents

(a) Hydrochloric acid, concentrated.

(b) Hydroxylamine Solution: Dissolve 10 g of $NH_2OH \cdot HCl$ in 100 ml distilled water.

(c) Ammonium Acetate Buffer Solution: Dissolve 250 g $NH_4C_2H_3O_2$ in 150 ml distilled water. Add 700 ml glacial acetic acid and dilute to 1 liter. (Since good grade $NH_4C_2H_3O_2$ contains a significant amount of iron too, new reference standards should be prepared with buffer solution preparation.)

(d) Phenanthroline Solution: Dissolve 0.1 g 1, 10-phenanthroline monohydrate, $C_{12}H_8N_2 \cdot H_2O$, in 100 ml distilled water by stirring and heating to 80° C; do not boil. Discard the solution if it darkens. Heating is not necessary if 2 drops of concentrated HCl are added to the distilled water. (Note that 1 ml of this reagent is sufficient for no more than 0.1 mg Fe).

(e) Stock Iron Solution:
(1) Use electrolytic iron wire, to prepare the solution. If necessary, clean the wire with fine sandpaper to remove any oxide coating and to produce a bright surface. Weigh 0.200 g wire and place in a 1-liter volumetric flask. Dissolve in 20 ml 6 N H_2SO_4 and dilute to the mark with iron-free distilled water.

(f) Standard Iron Solutions: These should be prepared the day they are used:

(1) Pipet 50.0 ml stock solution into a 1 liter volumetric flask and dilute to the mark with iron-free distilled water; 1.00 ml = 10.0 µg Fe.

(2) Pipet 5.0 ml stock solution into a 1 liter volumetric flask and dilute to the mark with iron-free distilled water; 1.00 ml = 1.00 µg Fe.

Procedure

Mix the sample thoroughly and measure 25 ml into a 50 ml volumetric flask. Add 2 ml concentrated HCl and 1 ml hydroxylamine solution. Also add 10 ml ammonium acetate buffer solution and 10 ml phenanthroline solution, and dilute to the mark with distilled water. Mix thoroughly and allow at least 10-15 minutes for maximum color development.

Preparation of Calibration Curve

Prepare a series of standards by accurately pipeting the calculated volumes of standard iron solutions (the weaker solution should be used to measure the 1-10 µg portions) into 50 ml volumetric flasks, diluting to 25 ml and carrying out the steps as in the procedure. For photometric measurement, the standards should be read against distilled water set at 100 per cent transmittance (zero absorbance) and a calibration curve plotted, including a blank.

The photometric analyses were conducted on a Beckman Spectrophotometer, Model DU, using 1 cm. and 5 cm cells. The phosphorus determination method was checked for iron interference by addition of known amounts of iron to the standard phosphate solutions.

The results showed that up to 1 mg of iron in the sample solution could be tolerated introducing a negative error not exceeding one per cent.

The interference of phosphate on the iron determination was investigated by Caldwell and Adams (10). They found that at 20 ppm of P_2O_5 the results were lower by 1.4 percent in the pH range from 2.0 - 7.0.

We checked the phosphate interference on the iron determination and found a negative error not exceeding two per cent at phosphate (as P) concentration up to 10 ppm.

In this work no samples (25 ml taken for determination) contained more than 10 ppm P.

EXPERIMENTAL RESULTS

Effect of pH

Figure 2 shows a plot of phosphate and iron removal (in percent) versus the pH of the solution using NaOH solution for pH adjustment. The initial pH of the KH_2PO_4 solution was 6.0 to 6.1. After addition and dissolving of $FeSO_4 \cdot 7H_2O$ the pH decreased to 5.5 to 5.6. No formation of precipitate was observed on addition and dissolution of $FeSO_4 \cdot 7H_2O$. Between pH of 7.1 to 7.6 the orthophosphate removal increases abruptly to approximately 80 percent, attaining a maximum removal of 87 percent at pH = 8.1 to 8.5. At pH higher than 8.5 the phosphate removal decreased rapidly to 16 percent at pH = 11.

The removal of added iron follows very closely the removal of ortho-phosphate up to pH = 8.1 and steadily increases with increase of pH up to 96.8 percent removal at pH = 9.8.

Figure 3 shows the results obtained for ortho-phosphate removal with ferrous sulfate from oxygen-free solutions when the pH was adjusted with calcium hydroxide suspension. The experimental points in the pH region from 7 to 8 showed considerable scattering but the general trend was obvious. The phosphate removal increased abruptly in this region. The curve showed an inflection point at pH = 9.0. This branch of the curve was very similar to that obtained by adjusting the pH with NaOH solution as shown in Figure 2. From the inflection point on, the phosphate removal increased attaining nearly 98 percent removal at pH = 10.4. The points shown in Figure 3 are those where the concentration of calcium in the supernatant solution was also determined.

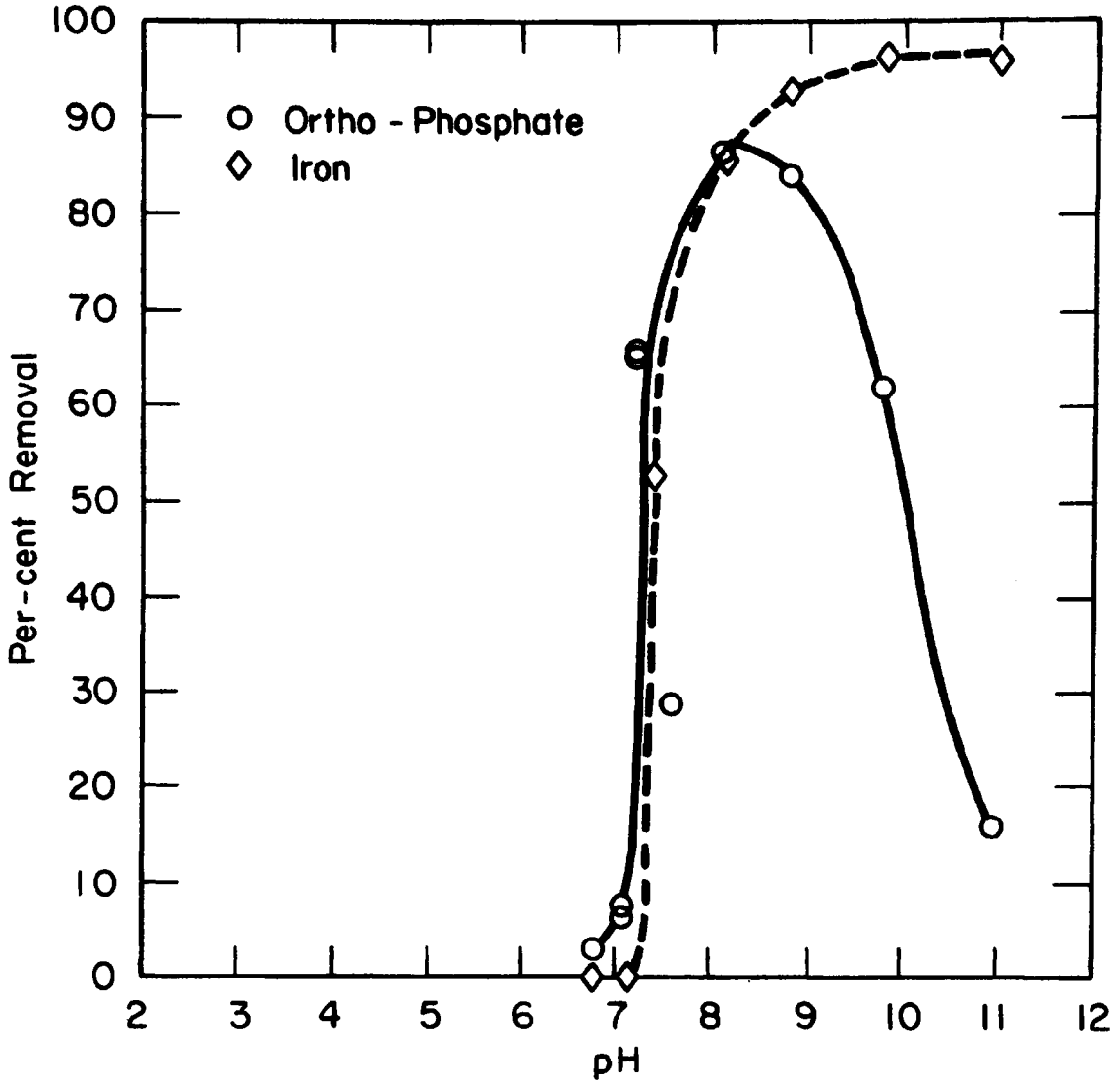


Figure 2. Per cent orthophosphate and iron removal vs pH. Initial orthophosphate concentration 35.0 mg/L PO_4 , $FeSO_4 \cdot 7H_2O$ 41.2 mg/L Fe. Mole ratio Fe:P = 2.0. 0.2 normal NaOH to adjust pH. Oxygen-free solutions. 5 minutes stirring at 100 RPM, 20 minutes stirring at 20 RPM. 1 hour settling time.

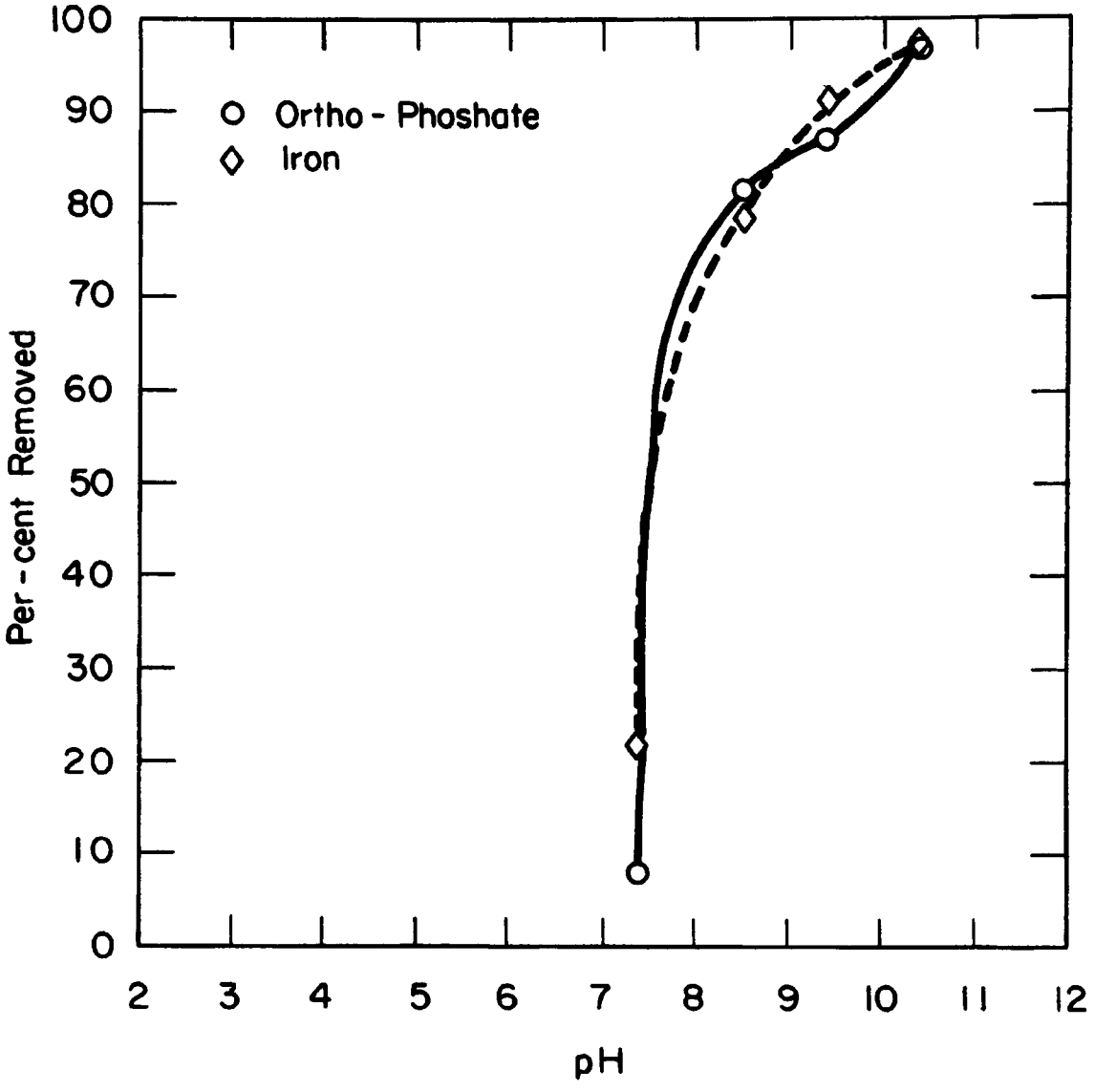


Figure 3. Per cent orthophosphate and iron removal vs pH. Initial orthophosphate concentration 35.0 mg/L PO_4, $FeSO_4 \cdot 7H_2O$ 41.2 mg/L Fe. Mole ratio Fe:P = 2.0. 0.2 normal $Ca(OH)_2$ suspension to adjust pH. Oxygen-free solutions. 5 minutes stirring at 100 RPM, 20 minutes stirring at 20 RPM. 1 hour settling time.

Table IV shows that the calcium content in the precipitate rapidly increased between pH = 8.5 to 9.4 and continued to increase with pH.

Effect of Molar Ratio of Iron to Phosphorus and Settling Time

Figure 4 shows the ortho-phosphate removal with addition of iron. The phosphate removal of 84.7 percent at a mole ratio of Fe:P = 1.5 increases rapidly to 92.1 percent at a mole ratio of Fe:P = 3.2 and then increases nearly linearly with iron concentration to 98.4 percent at a mole ratio of Fe:P = 8.1.

Figure 5 shows the plot of phosphate removal in mg-moles per mg-moles of iron added as a function of the concentration of phosphate in mg-moles left in the supernatant solution. A break in the curve is observed at mole ratio of iron added to total phosphate in original solution of approximately six.

Figure 6 shows a plot of the residual concentration of phosphate and iron in the supernatant solution vs. time at mole ratios of Fe to P of 2.0, 1.5, and 1.0. At mole ratio of Fe to P of 2.0 and 1.5 the equilibirum is approached in 1 to 2 hours, but at Fe to P mole ratio of 1.0, the equilibrium is not yet attained after 21 hours reaction and settling time.

TABLE IV. INCREASE OF CALCIUM IN PHOSPHATE PRECIPITATE WITH INCREASING pH*

Run No.	pH	Ca^{++} added (mg)	Ca^{++} found in solution (mg)	Ca^{++} in precipitate (mg)
psN1	7.4	8.72	8.35	0.37
psN2	8.5	12.90	12.42	0.48
psN3	9.4	15.51	12.90	2.61
psN4	10.4	22.77	18.48	4.29

*To 600.0 ml solution of 35.0 mg/liter PO_4 (11.43 mg/liter P) as KH_2PO_4, $FeSO_4 \cdot 7H_2O$ was added to concentration of 41.1 mg/liter as Fe.

Approximately 0.04 normal solution of $Ca(OH)_2$ was used to adjust the pH. No oxygen was present in the solutions.

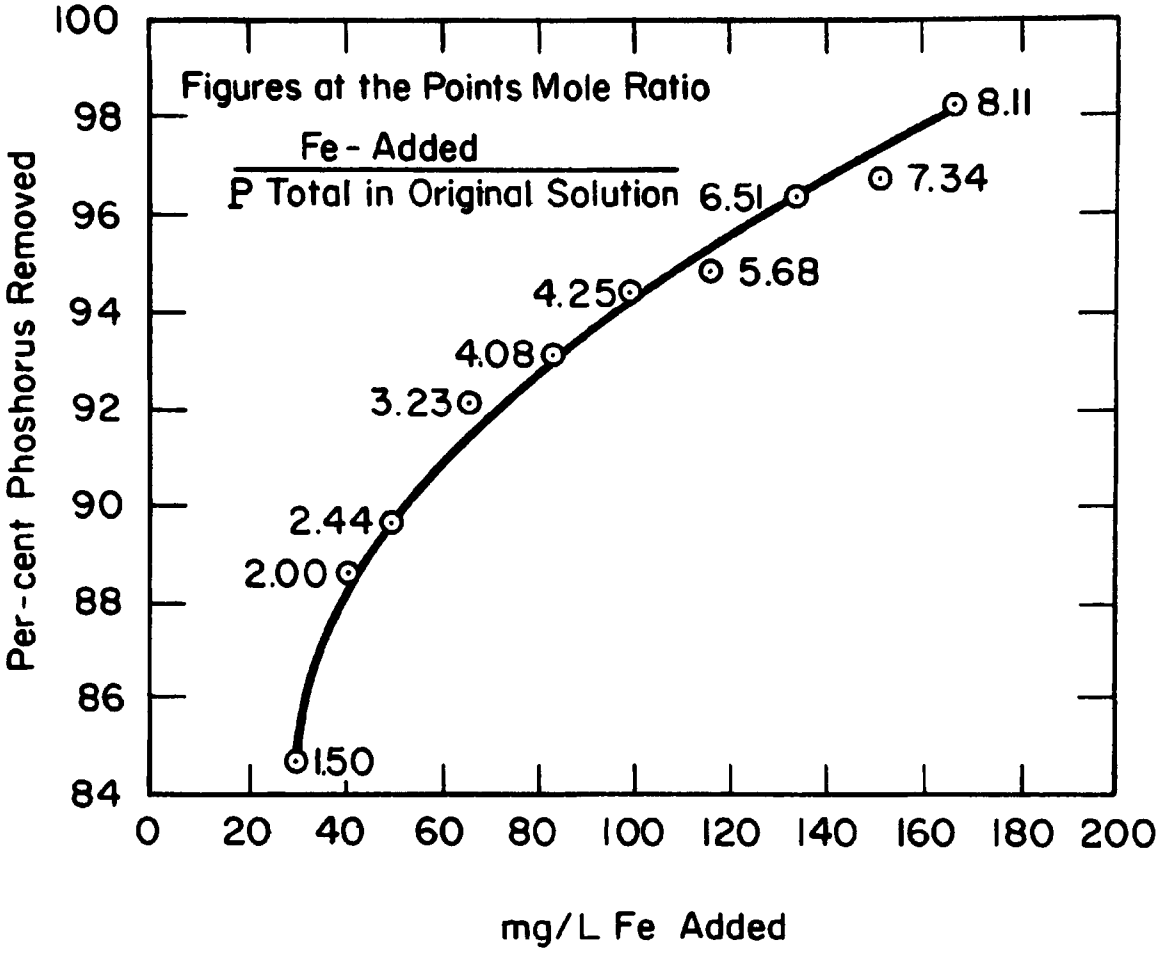


Figure 4. Per cent orthophosphate removed vs mg/L Fe added as $FeSO_4$ $7H_2O$. Initial orthophosphate concentration 35.0 mg/L PO_4. pH =7.5 adjusted with 0.2 normal $Ca(OH)_2$ suspension. 5 minutes stirring at 100 RPM, 5 minutes stirring at 20 RPM. 20 minutes settling time. Oxygen-free solutions.

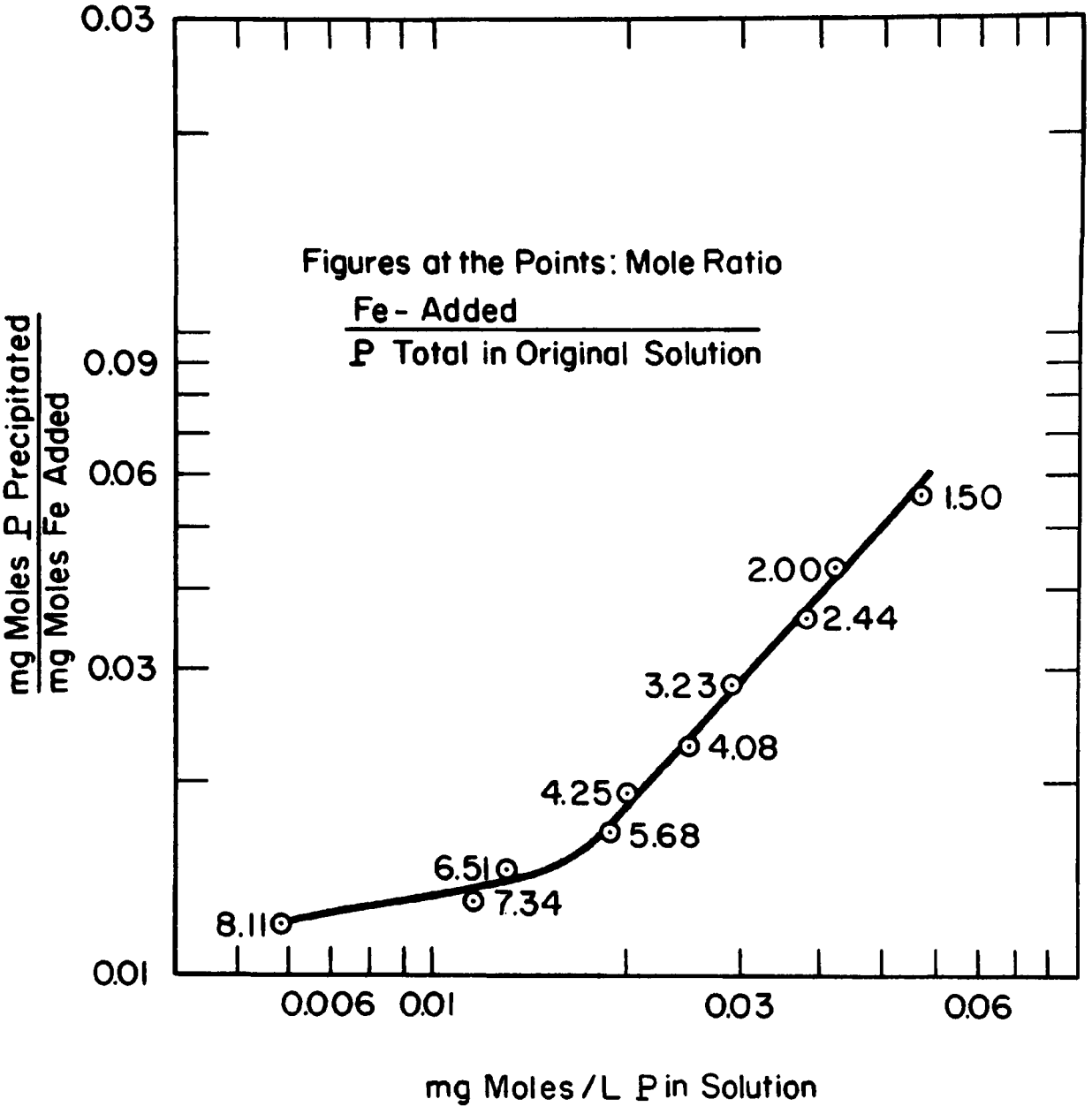


Figure 5. Mg-moles P precipitated per 1 mg-mole Fe added as $FeSO_4$ $7H_2O$ vs mg-moles P uf in solution. Initial orthophosphate concentration 35.0 mg/L PO_4 (0.3685 mg-moles P). Fe added as $FeSO_4$ $7H_2O$. pH=7.5 adjusted with 0.2 normal $Ca(OH)_2$ suspension. 5 minutes stirring at 100 RPM, 5 minutes stirring at 20 RPM. 20 minutes settling time. Oxygen-free solutions.

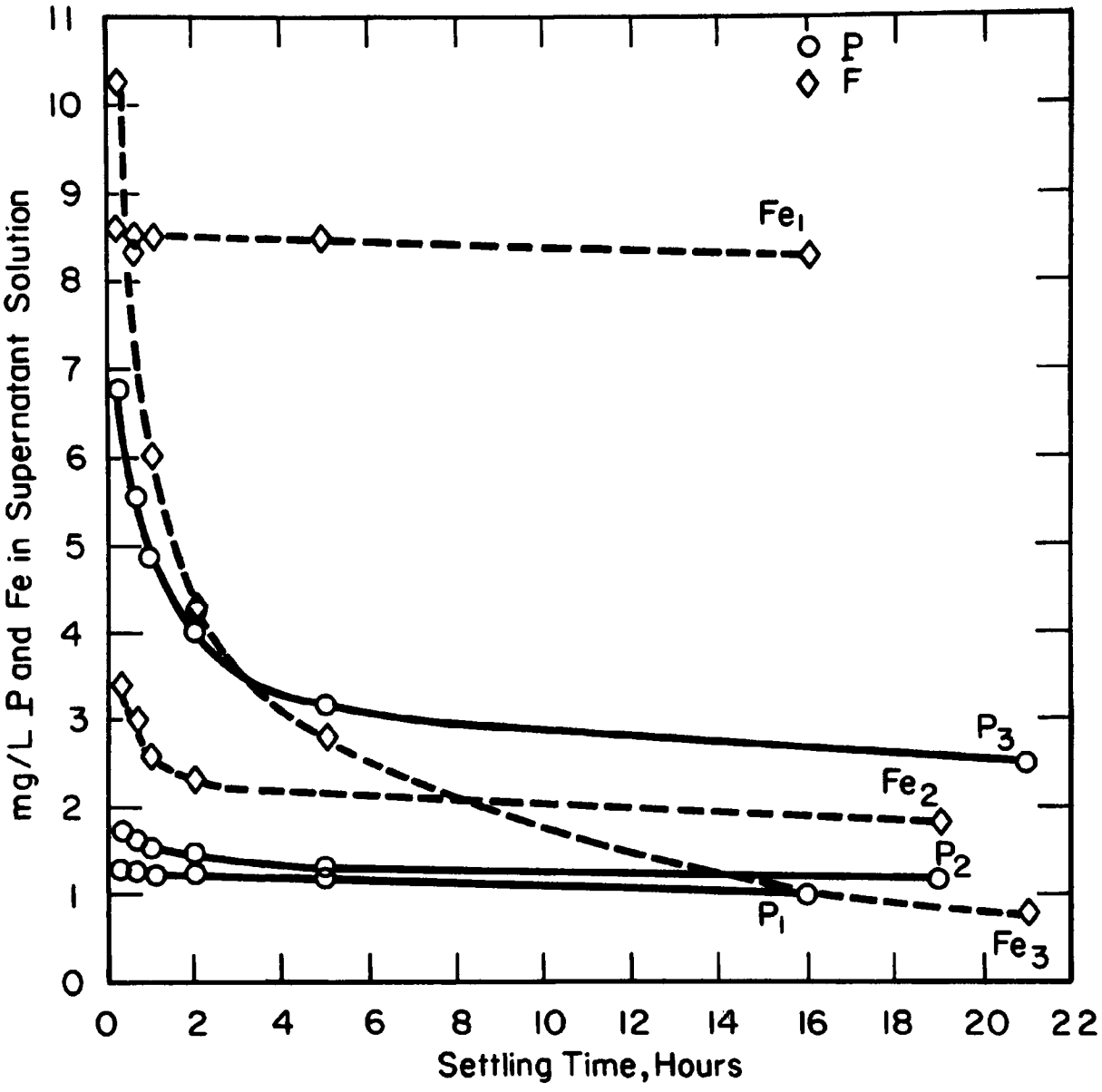


Figure 6. Concentration of phosphorus and iron (mg/L) in supernatant vs settling time. Initial orthophosphate concentration 35.0 mg/L PO_4 Fe added as $FeSO_4$ $7H_2O$. pH=8.5 adjusted with 0.2 normal $Ca(OH)_2$ suspension. Oxygen-free solutions.

Curves: P_1 Fe_1 mole ratio Fe:P = 2.0
P_2 Fe_2 mole ratio Fe:P = 1.5
P_3 Fe_3 mole ratio Fe:P = 1.0

DISCUSSION OF RESULTS

The ortho-phosphate removal from oxygen-free ortho-phosphate (KH_2PO_4) solutions with ferrous sulfate ($FeSO_4 \cdot 7H_2O$) is strongly pH dependent as illustrated by Figures 2 and 3. The formation of ferrous phosphate precipitate, occurs below a pH of 7, but the coagulation and flocculation rates are slow. At pH of 7.to 8 the coagulation and flocculation is spontaneous and the efficiency of phosphate removal in this pH interval is determined largely by the coagulation, flocculation and settling rates of the ferrous phosphate precipitate.

Work on the effect of pH on the efficiency of phosphate removal was also conducted in the presence of 1 ppm Purifloc A-23, a high molecular weight anionic polyelectrolyte manufactured by Dow Chemical Company. Essentially the same results were obtained at a settling time of 15 minutes as compared with one hour settling time without addition of Purifloc A-23. On the basis of visual observation and results obtained it was concluded that the presence of Purifloc A-23 significantly increased the flocculation rate and consequently the settling rate of the precipitate, but did not increase the phosphate removal which is controlled primarily by pH. The results obtained by froth-flotation (see Section VI), showed a very narrow pH range for maximum phosphate removal around pH = 7.

The excess of ferrous iron left in solution follows the same pattern as the solubility of ferrous hydroxide as determined by W. Stumm (11). Deviations are toward higher solubility which is not surprising because the measurements were taken after relatively short settling times and are not the equilibrium values.

The rapid decrease of phosphate removal in the pH range of 8.5 to 11 using sodium hydroxide for pH adjustment is attributed to the conversion of ferrous phosphate to ferrous hydroxide and formation of soluble sodium phosphate. The process may be described by the reaction:

$$Fe_3(PO_4)_{2(s)} + 6\ OH^- \rightleftharpoons 3Fe(OH)_{2(s)} + 2\ PO_4^{-3}$$

The phosphate removal using lime, ($Ca(OH)_2$) for pH adjustment shows an inflection point at a pH of approximately nine (Figure 3) and continues to increase at higher pH values. Table IV shows that from a pH of 9 the calcium content of the precipitate increases rapidly with increasing pH.

Up to the inflection point the phosphate removal is accomplished almost entirely by precipitation as ferrous phosphate; above the inflection point the phosphate is precipitated as a calcium phosphate, probably as hydroxyapatite ($Ca_{10}(OH)_2(PO_4)_6$)which forms at pH > 7. Calculations show that the amount of calcium in the phosphate precipitate at higher pH is much larger than is required to precipitate the phosphate which was not precipitated by ferrous sulfate. This can be accounted for by the reaction:

$$3Fe_3(PO_4)_2 + 10Ca(OH)_2 \rightleftharpoons 9Fe(OH)_2 + Ca_{10}(OH)_2(PO_4)_6.$$

The efficiency of phosphate removal increased with increased amounts of ferrous sulfate added as shown in Figures 4 and 5.

In the range of mole ratio of ferrous sulfate added to the phosphate present in original solution from 1.5 to 5.7.the mole ratio of Fe to P in the precipitate, as calculated from the analysis of the supernatant solution, was very close to 1.5 indicating, the formation of a ferrous phosphate compound.

R. F. Wukasch (5) found vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) in sludges formed by removal of phosphates from water with ferrous chloride by x-ray diffraction analysis.

The plot of mg-moles phosphorus precipitated per mg-mole of ferrous iron added vs. mg-moles phosphorus left in solution in logarithmic coordinates is shown in Figure 5. This kind of plot should give a straight line in the case of a chemical reaction or adsorption representable by Freundlich adsorption isotherm. The change of slope of the curve occurs at a mole ratio of ferrous iron added to the phosphorus in original solution of approximately six. The change in slope indicates a change in the mode of phosphate removal. From a ratio of Fe to P of 1.5 up to 6, the phosphate is removed as ferrous phosphate (and probably small amounts by adsorption on the formed precipitate also). From Fe to P ratio above six, the phosphate may be removed by: (a) adsorption; (b) decrease of solubility caused by high concentration of ferrous ions in solution; (c) precipitation as calcium phosphate due to high concentration of calcium ions; or (d) combination of these three possibilities. The decrease of calcium in the solution strongly supports the assumption that the phosphate is removed as calcium phosphate.

Figure 6 shows the effect of settling time on the residual concentration of iron and phosphorus at Fe to P mole ratio of 2.0, 1.5 and 1.0 (Fe added to P in original solution). At Fe to P mole ratio of 2.0 the residual phosphorus and iron concentration remains practically constant after three hours of settling. The estimated mole ratio of Fe to P in the precipitate was 1.77. The higher Fe to P ratio in the precipitate than required by the formula $Fe_3(PO_4)_2$ is probably due to the concentration of ferrous iron. The concentration of ferrous iron in solution is close to the solubility of $Fe(OH)_2$ and suggests that some $Fe(OH)_2$ is co-precipitated with the ferrous phosphate. At Fe to P mole ratio of 1.5 the mole ratio of Fe to P in the precipitate was 1.5 and the residual phosphorus and iron concentration remained constant after three hours of settling.

At Fe to P mole ratio of 1.0 the Fe to P mole ratio in the precipitate was 1.22 and the residual phosphorus and iron concentration was still decreasing after 21 hours settling time. The estimated mole ratio of Fe to P in the precipitate after 20 minutes settling time was 1.5, assuming that all calcium in precipitate was combined with phosphorus as $Ca_3(PO_4)_3$. The slow approach to equilibrium of Fe and P concentrations in the supernatant solution indicates a slow reaction rate of solid ferrous phosphate formation. These results also strongly support the conclusion that a definite ferrous phosphate compound having a Fe to P mole ratio of 1.5 is formed.

CONCLUSIONS

(1) The maximum removal of ortho phosphate from oxygen-free phosphate solutions with ferrous sulfate occurs at a pH = 7 to 7.5.

If ferrous sulfate is applied in excess of Fe to P mole ratio of 1.5, the residual concentration of ferrous iron in solution decreases with increasing pH.

(2) Lime ($Ca(OH)_2$) is superior to NaOH for pH adjustment because the coagulation, flocculation,and sedimentation velocities are higher with lime and because no decrease of phosphate removal is observed at higher than pH = 7.0.

(3) The removal of phosphate increases with increasing mole ratio of Fe to P, but economical considerations suggest a mole ratio between 1.5 and 2.0.

The residual phosphorus concentration of Fe to P mole ratio of 1.5 and 2.0 (pH = 7.5; initial phosphorus concentration 11.43 mg/l) was 1.75 and 1.30 mg/l corresponding to 84.7 and 88.5 percent phosphorus removal respectively. The corresponding ferrous iron residual concentration was 3.4 and 8.6 mg/l corresponding to 89.0 and 79.1 percent iron removal respectively.

(4) The phosphate is precipitated in the form of ferrous phosphate with a mole ratio of Fe to P close to 1.5. At pH above 7.5 using $Ca(OH)_2$ for pH adjustment, phosphate is also precipitated as calcium phosphate.

(5) The formation of the precipitate is spontaneous at Fe to P ratio of 1.5 to 2.0 and above. Using $Ca(OH)_2$ for pH adjustment, the coagulation, flocculation and settling is fast and yields a clear supernatant.

SECTION 6

PRECIPITATION OF PHOSPHATE FROM OXYGEN-CONTAINING PURE PHOSPHATE SOLUTIONS WITH FERROUS SULFATE AND SEPARATION OF THE PRECIPITATE BY SEDIMENTATION

Werner Stumm (11) showed that improved phosphate removal by ferric iron can be achieved when ferrous iron is added to the phosphate solution and subsequently oxygenated in situ. Stumm's experimental results showed that efficiency of phosphate removal was enhanced by utilization of the homogeneous precipitation technique (generation of Fe(III) in situ) in the pH interval from 5.0 to 6.5. An exception was observed at pH = 7.0 (the highest pH reported). Stumm also emphasizes that a distinction must be made between equilibrium and kinetics. At lower pH values the hydrolysis of Fe(III) is decelerated and the precipitation of phosphate is enhanced; on the other hand, the osygenation of Fe(II) decreases rapidly with decrease of pH. The oxygenation rate decreases by a factor of 100 for each unit decrease in pH below pH = 6. According to Stumm, the reaction rate given by the equation:

$$\frac{-d(FeII)}{dt} = K\,(Fe(II))\,(OH^-)^2\,P_{O_2}$$

is first order in (Fe(II)) and P_{O_2} and second order in (OH^-) at pH = 4.5 and up to 6. The oxygenation rate is also catalytically enhanced in the presence of phosphate (12, 13).

Considering the results of Stumm's (11) work and the results obtained from this study as discussed in Section 4 and 4, a mechanism of the process was assumed as an aid to planning this work and to explain the results of experimental data. A discussion of the validity of the assumptions will be presented later in this chapter.

The assumed mechanism is as follows:

At pH higher than approximately 6 the formation of solid ferrous phosphate and the oxygenation of ferrous iron and formation of ferric phosphate in solution proceeds simultaneously. The efficiency of phosphate removal is affected by the oxygenation rate of ferrous iron in solution. At slower oxygenation rates, higher removal is attained because the hydrolysis of ferric iron is slower than the ionic reaction to form ferric phosphate and therefore a higher percentage of the ferric ions formed by the oxygenation of ferrous iron is used to precipitate phosphate. The oxygenation rate depends on pH, oxygen concentration, ferrous iron concentration and phosphate concentration.

The ionic reaction of ferrous phosphate formation is very fast and proceeds according to the stoichiometric requirements of the overall reaction:

$$3Fe^{+2} + 2\ PO_4^{-3} \rightarrow Fe_3(PO_4)_{2(S)}$$

Ferrous iron in solution is oxygenated <u>in situ</u> to ferric iron which simultaneously reacts with phosphate remaining in solution to form ferric phosphate. Part of the ferric iron may hydrolyze (at a slower rate than the ferric phosphate formation reaction) to ferric hydroxide according to the overall reactions:

$$(a)\quad Fe^{+2} + 1/4\ O_2 + H^+ + PO_4^{-3} \rightarrow FePO_{4(s)} + 1/2\ H_2O$$

$$(b)\quad Fe^{+2} + 1/4\ O_4 + 2\text{-}1/2\ H_2O \rightarrow Fe(OH)_{3(s)} + 2H^+$$

A slower reaction rate of the oxygenation step will result in a decrease in the rate of formation of ferric hydroxide, (reaction (b)) and favor the formation of ferric phosphate, (reaction(a)) because of the limited number of ferric ions present at any one time which will react first with the phosphate (reaction(a)). The final concentration of phosphate in solution is reduced by the oxygenation step of ferrous iron and depends on the ferric phosphate solubility.

Other factors influence the final composition of the solid phase, as shown below:

(1) According to the overall reaction

$$2Fe_3(PO_4)_{2(s)} + 1\text{-}1/2\ O_2 + 3H_2O \rightarrow 4FePO_{4(s)} + 2Fe(OH)_{3(s)}$$

the formed solid ferrous phosphate is oxygenated to ferric phosphate and ferric hydroxide and both remain in solid phase due to low solubility of $FePo_4$ and $Fe(OH)_3$.

(2) If an excess of ferrous iron is present it may be in solution or precipitaed as ferrous hydroxide depending on the conditions of the experiment (pH). The ferrous hydroxide formed is oxygenated to ferric hydroxide according to the equation

$$Fe(OH)_{2(s)} + 1/4\ O_2 + 1/2\ H_2O \rightarrow Fe(OH)_{3(s)}$$

and remains in solid phase.

EXPERIMENTAL PROCEDURE

Reagents

Phosphate stock solution was prepared by dissolving 4.0118g KH_2PO_4 (Reagent grade, B and S) in 1000 ml of distilled water 10 ml of this solution diluted to 800 ml produced phosphate solution containing 35.0 mg/l PO_4.

Approximately 0.2 normal $Ca(OH)_2$-suspension was prepared by shaking 0.797g $Ca(OH)_2$ (Reagent grade, B and S, 93%) with 100 ml CO_2-free distilled water in a closed 200 ml polyethylene bottle. The suspension was prepared as needed.

Weighed quantities of $FeSO_4 \cdot 7\ H_2O$ (Reagent grade, B and S, 99.5%) were added to the phosphate solution to attain the desired iron concentration.

Procedure and Equipment

To a measured voluem of distilled water in a 1000 ml beaker was added an accurately measured volume of phosphate stock solution to obtain the desired phosphate concentration in 800 ml of final volume. The solution was stirred on a Phipps and Bird 6 gang variable speed stirrer with 1" x 3" blades at 100 RPM. A weighed quantity of $FeSO_4 \cdot 7\ H_2O$ was added and quickly dissolved, and the pH was adjusted with approximately 0.2 normal $Ca(OH)_2$ suspension. These operations were completed in 5 minutes. The stirring speed was reduced to 20 RPM and stirred for 20 minutes. The suspension then was allowed to settle. After a specified

settling time, samples were taken for phosphate and iron determination in the supernatant. A series of runs were made removing the solids by filtration (Figures 7 and 8). To the phosphate solution $FeSO_4 \cdot 7 H_2O$ was added, dissolved, and the pH adjusted with the $Ca(OH)_2$-suspension by stirring at 100 RPM. This was accomplished in 5 minutes. The stirring speed was reduced to 20 RPM and continued for 20 minutes. The solutions were filtered immediately on a Whatman No. 42 filter paper, and samples were taken for phosphate and iron determination.

The analysis was performed according to the procedures described in Section 5.

The pH was measured with a Sargent Model LS pH-meter and Sargent S-30072-15 pH combination electrode.

Oxygen was determined with a Yellow Spring Instrument Co. Model 51 oxygen meter and probe.

Calcium in the supernatant solution was determined using a Perkin-Elmer Model 303 atomic absorption spectrophotometer. In the runs where calcium was determined in the supernatant solution, accurately weighed quantities of $Ca(OH)_2$ were suspended in small volume of water (to yield approximately 0.2 normal suspension) and quantitatively transferred to the phosphate-iron solution.

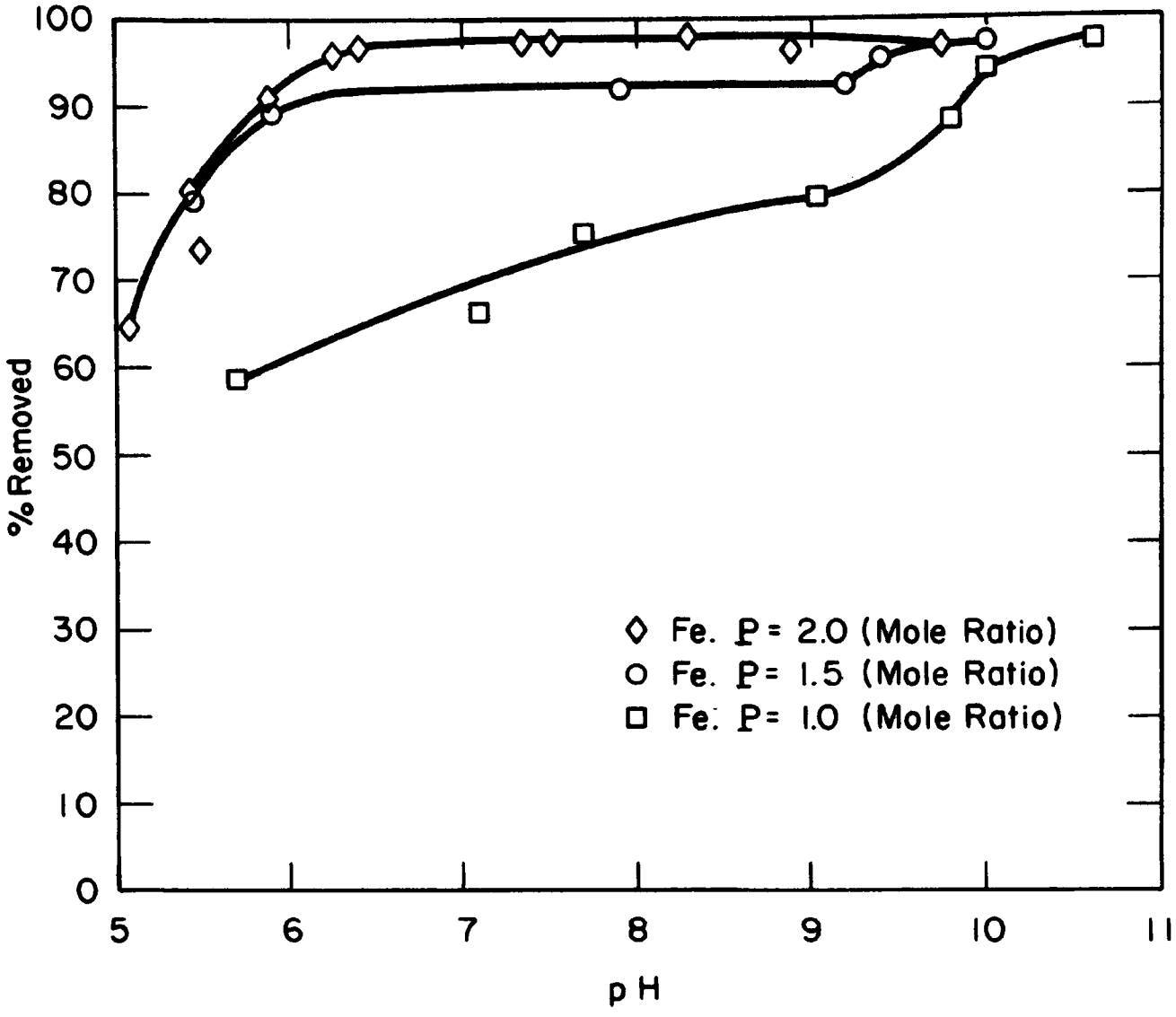


Figure 7. Phosphate removal in per cent vs pH. Initially solutions saturated with air. Initial phosphate solution 35.0 mg/L PO_4 $FeSO_4 \cdot 7H_2O$ added. pH adjusted with 0.2 normal $Ca(OH)_2$ suspension. 5 minutes mixing at 100 RPM, 20 minutes stirring at 20 RPM. Filtered on Whatman No. 42 filter paper.

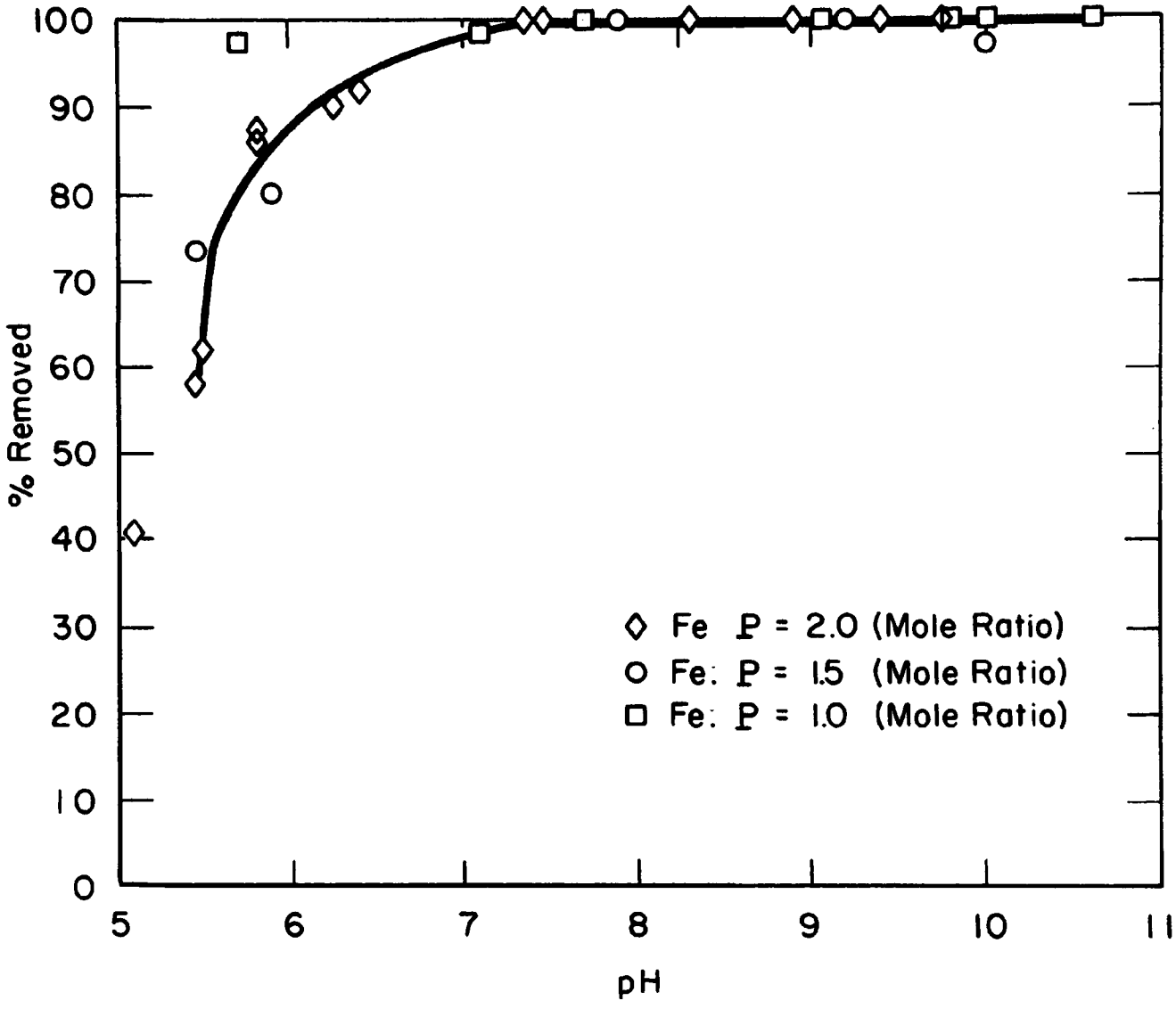


Figure 8. Per cent iron removal vs pH. Initially solutions saturated with air. Initial phosphate concentration 35.0 mg/L. $FeSO_4$ $7H_2O$ added. pH adjusted with 0.2 normal $Ca(OH)_2$ suspension. 5 minutes mixing at 100 RPM, 20 minutes stirring at 20RPM. Filtered on Whatman No. 42 filter paper.

RESULTS AND DISCUSSION

1. Effect of pH, Oxygen and Excess of Ferrous Iron.

Figure 7 shows a plot of phosphate removal vs pH at Fe to P mole ratio of 2.0, 1.5, and 1.0.

The initial phosphate solution contained 35.0 mg/l PO_4. The filtered supernatant was analyzed. All solutions contained an excess of oxygen required for complete oxygenation of ferrous iron.

The results obtained at mole ratio of Fe:P = 2.0 and 1.5 and pH lower than 6 show an apparent decrease of phosphate removal with decreasing pH. Oxygen measurements showed that the oxygen consumption was less than required for complete oxygenation of the ferrous iron present. Also, ferrous iron was found in the filtered supernatant. Figure 8 shows that the iron content of the supernatant increases with decreasing pH (from pH = 7 and lower) and is due to the higher solubility of ferrous iron. The oxygenation rate is slower at lower pH and shows that 25 minutes was too short a period of time to accomplish complete oxygenation of ferrous iron and therefore the phosphate removal decreased with decreasing pH. This is to be expected according to the assumed mechanism of the process.

The curve at Fe:P = 2.0 shows the highest phosphate removal at pH = 6.5 and higher. Mole ratio Fe:P = 1.5 is the minimum required to completely precipitate the phosphate as ferrous phosphate ($Fe_3(PO_4)_2$). The excess of ferrous iron is oxygenated *in situ* and reacts with the phosphate left in solution to form ferric phosphate and ferric hydroxide. The precipitated ferrous phosphate is simultaneously oxygenated to ferric phosphate and ferric hydroxide and remains in the solid phase.

The overall phosphate removal from oxygen-containing solutions should be higher than when phosphate is removed from oxygen-free solution. Figure 7 shows a phosphate removal of 98.2 percent at pH = 8.3 and Fe:P = 2.0. Figure 6 shows a phosphate removal of 89.2 percent calculated on a percent basis at pH = 8.4, Fe:P = 2.0, and 1 hour settling time from oxygen-free phosphate solutions. The phosphate removal was improved by 9 percent and the residual concentration of P was 0.21 mg/l as compared with 1.30 mg/l from Figure 6. This was also expected according to the assumed mechanism. The runs made at Fe:P = 1.5 follow the same pattern as at Fe:P = 2.0 except that the removal is lower. A Fe:P = 1.5 is required by the stoichiometry of the reaction. At Fe:P =1.5, most of the ferrous iron is precipitated as ferrous phosphate and little is left in solution for oxygenation in situ. Figure 6 shows a residual concentration of phosphate of 1.55 mg/l corresponding to a removal of 86.4 percent at pH = 8.8 and one hour settling time. Figure 7 shows a P residual concentration of 0.85 mg/l corresponding to a removal of 92.4 percent or an improvement of phosphate removal of 6 percent as compared with the removal from oxygen-free solution. The improvement is relatively less at Fe:P = 1.5 compared to Fe:P = 2.0 (9 percent), as was expected.

The results of runs shown in Figure 7 were obtained by filtration of the suspension and compared to results obtained by sedimentation as shown in Figure 6. The phosphate removal from oxygen-containing solution was also conducted by separation of the solids by sedimentation. The results are shown on Figures 9 and 10 and are identical, within the accuracy of the experiments, to the results of Figure 7 and 8 at Fe:P = 2.0 and 1.5.

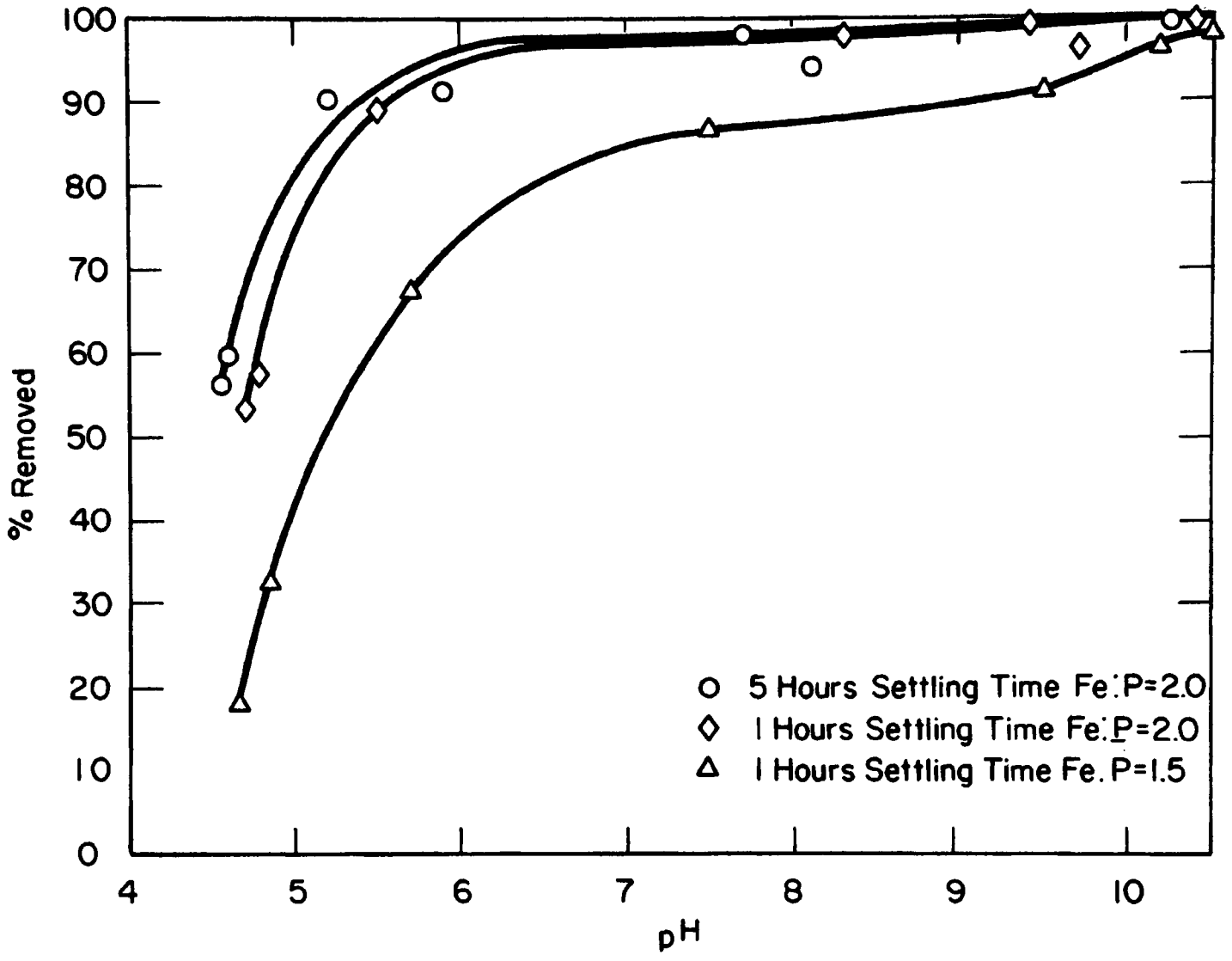


Figure 9. Phosphate removal in per cent vs pH. Solids removed by settling. Initially solutions saturated with air. Initial phosphate concentration 35.0 mg/L P. Solid $FeSO_4 \cdot 7H_2O$ added. pH adjusted with 0.2 normal $Ca(OH)_2$ suspension. 5 minutes mixing at 100 RPM, 20 minutes stirring at 20 RPM.

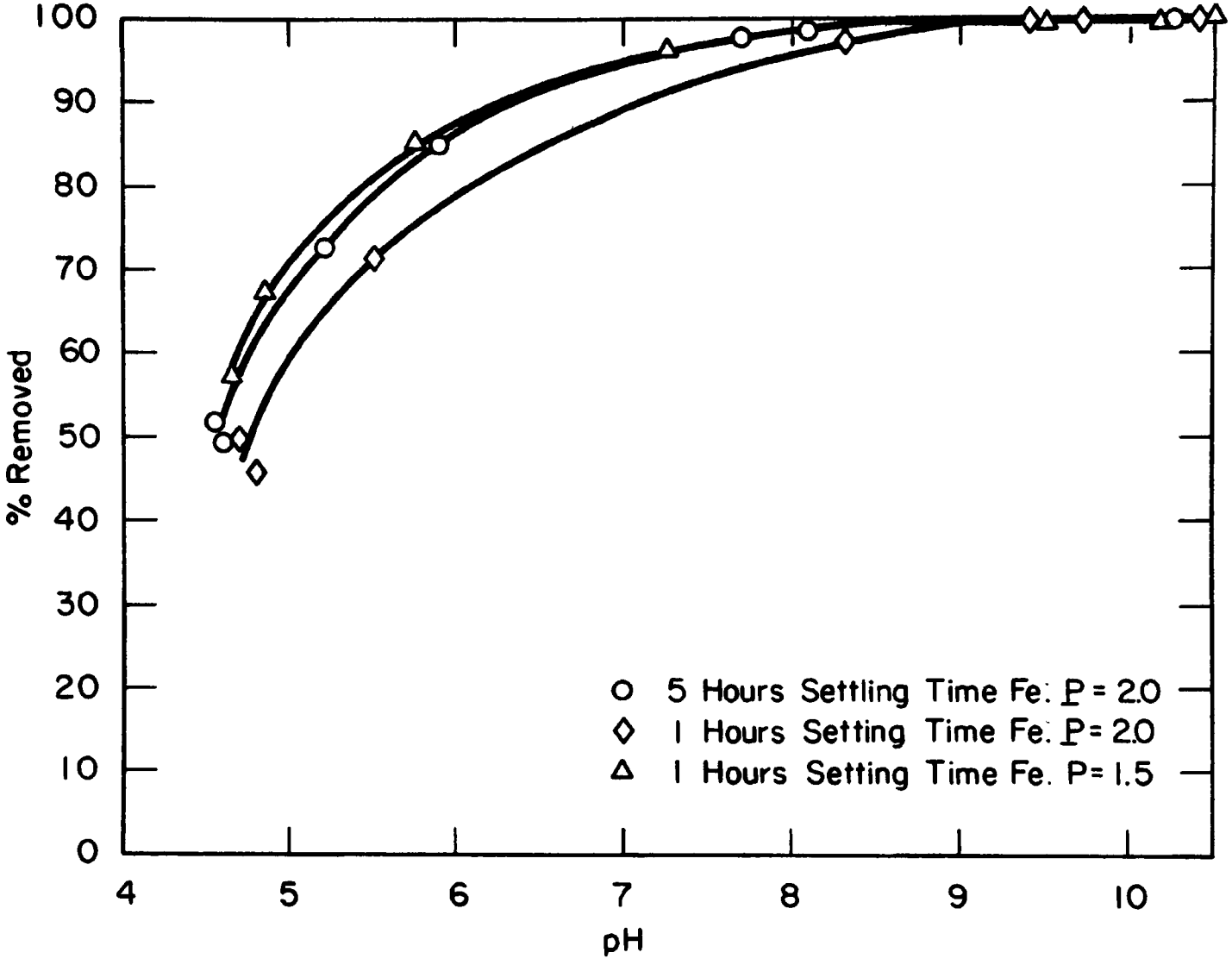


Figure 10. Per cent iron removal vs pH. Solids removed by settling. Initially solutions saturated with air. Initial phosphate concentration 35.0 mg/L PO_4 . Solid $FeSO_4 \cdot 7H_2O$ added. pH adjusted with 0.2 normal $Ca(OH)_2$ suspension. 5 minutes mixing at 100 RPM, 20 minutes stirring at 20 RPM.

The residual concentration of iron at pH = 7 and higher was very low (0.05 mg/l) as shown on Figure 8. This was expected because of much lower solubility of $Fe(OH)_3$ compared to $Fe(OH)_2$. The solubility of $Fe(OH)_2$ is strongly dependent on pH and rapidly decreases with increase of pH (11). The residual concentration of iron in the supernatant solutions containing no oxygen was 8.4 mg/l at Fe:P = 2.0 and pH = 8.45, and 2.6 mg/l at Fe:P = 1.5 and pH = 8.8.

In all runs at pH = 6.5 and higher the oxygen concentration rapidly decreased during the first 3 to 4 minutes and the oxygen consumption approached the theoretical requirements for complete oxygenation of the ferrous iron. Also most of the ferrous iron and phosphate were precipitated. Therefore, the oxygenation rate, after the initial period, was controlled by the oxygen concentration remaining in solution. The oxygen concentration in solution increased with decreasing initial ferrous iron concentration and subsequently the oxygenation rate should increase. According to the assumed mechanism the phosphate removal should decrease with decreasing initial ferrous iron concentration, the Fe:P ratio and other variables being identical. Figure 11 shows a plot of phosphate and iron removal vs. pH. The initial phosphate concentration was 17.5 mg/l PO_4 and Fe:P = 2.0. The residual concentration of P and Fe was higher than in runs where the initial concentration of phosphate was 35 mg/l (Figure 7) and is in agreement with the assumed mechanism. It should be mentioned that the system (17.5 mg/l PO_4) had a tendency to form colloidal dispersions and the poor coagulation properties were attributed to the lower concentration of other ions, particularly calcium.

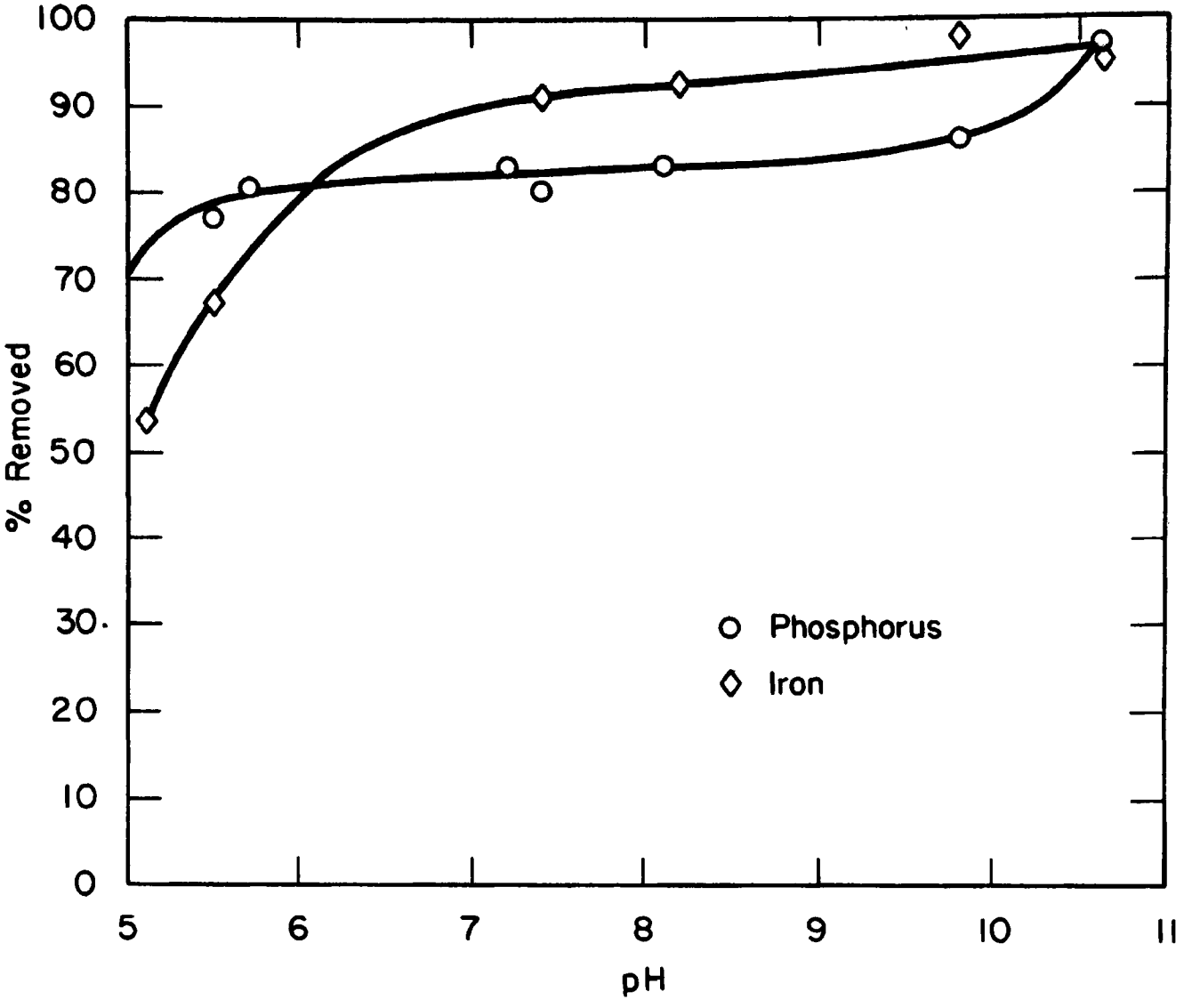


Figure 11. Phosphate and iron removed in percent vs pH. Initially solutions saturated with air. One hour settling time. Initial phosphate concentration 17.5 mg/L PO_4. Mole ratio Fe:P = 2.0. Solid $FeSO_4 \cdot 7H_2O$ added. pH Adjusted with 0.2 normal $Ca(OH)_2$ suspension. Five minutes mixing at 100 RPM, 20 minutes stirring at 20 RPM.

The results presented by Figures 7 and 8 at pH 6 to 9 and Fe:P = 1.0 show a poor phosphate removal. If the phosphate was removed as ferric phosphate by generation of ferric iron in situ, more efficient removal would be expected than if directly precipitated with ferric iron. The experiments show this to be true. Figure 12 curve 3 shows that the phosphate removal with ferric sulfate at Fe:P = 1.0 and pH = 7.4, after one hour settling time, was 88.5 percent (residual concentration 1.32 mg/l) of the theoretical value. The phosphate removal according to Figure 7 was 99 percent of theoretical (66.2 percent at Fe:P = 1.0 and pH = 7.1 as compared to a maximum [theoretical] removal of 66.7 percent). If ferrous phosphate was first formed and then oxygenated the theoretical removal should be 66.7 percent which is in agreement with the experimental results.

The results discussed so far were obtained by adjusting the pH of the phosphate-iron solution by addition of a $Ca(OH)_2$ suspension to the solution at lower pH. The addition of $Ca(OH)_2$ suspension was completed in 1 to 2 minutes and considering the mixing effects and dissolution of $Ca(OH)_2$ particles, the process should be slower than the ionic reaction of ferrous phosphate formation. The solubility of $Fe(OH)_2$ decreases with increasing pH and thus also favors the formation of ferrous phosphate which reduces the formation of $Fe(OH)_2$ precipitate. When the pH of the phosphate solution is adjusted before the addition of ferrous iron, a larger fraction of the ferrous iron is converted to $Fe(OH)_2$. Consequently, a lower phosphate removal is expected. The experimental results shown in Figure 13 confirm the expected results.

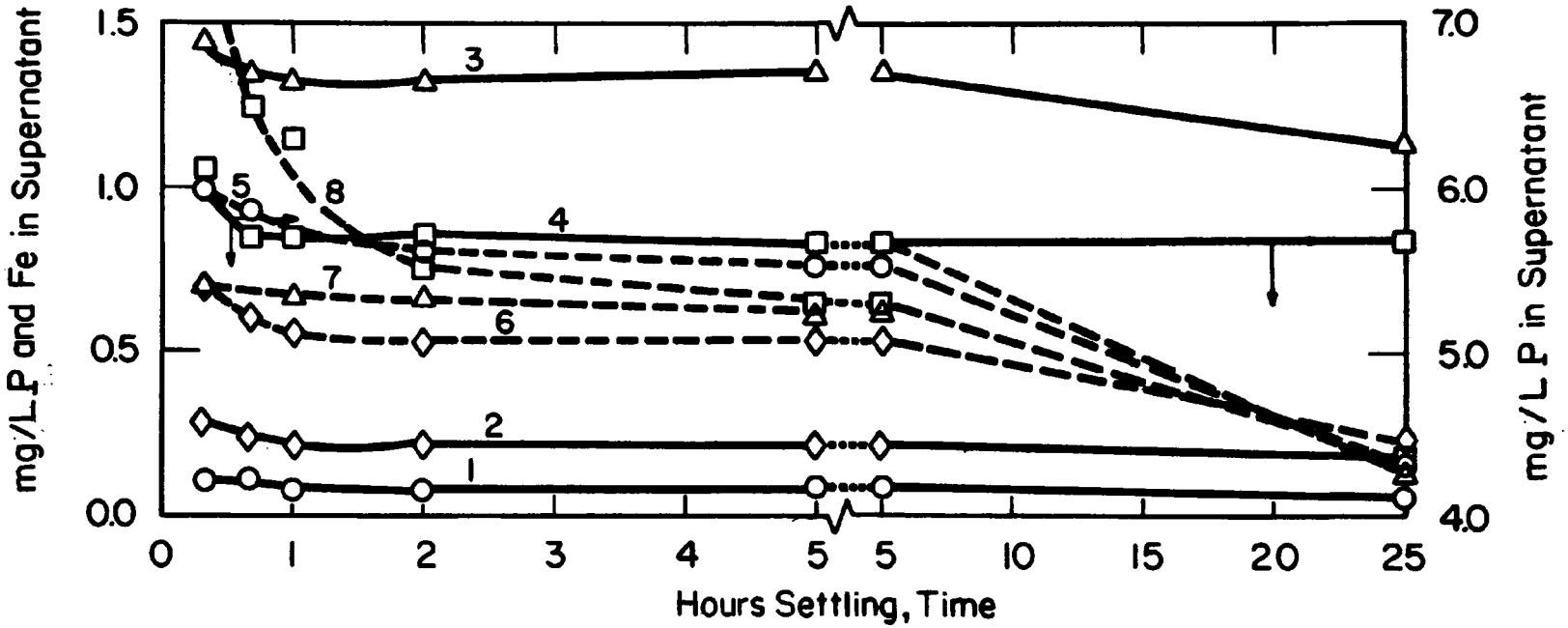


Figure 12. Residual concentration of phosphate (as P) and iron (Fe) in supernatant vs time, hours. Initial phosphate concentration 35.0 mg/L PO_4 . $Fe_2(SO_4)_3$ solution added. pH = 7.0 to 7.3 adjusted with 0.2 normal $Ca(OH)_2$ suspension. Initially solutions saturated with air. 5 minutes mixing at 100 RPM, 20 minutes stirring at 20 RPM.

Curves: 1 and 5: P and Fe, mole ratio Fe:P = 2.0
2 and 6: P and Fe, mole ratio Fe:P = 1.5
3 and 7: P and Fe, mole ratio Fe:P = 1.0
4 and 8: P and Fe, mole ratio Fe:P = 0.5

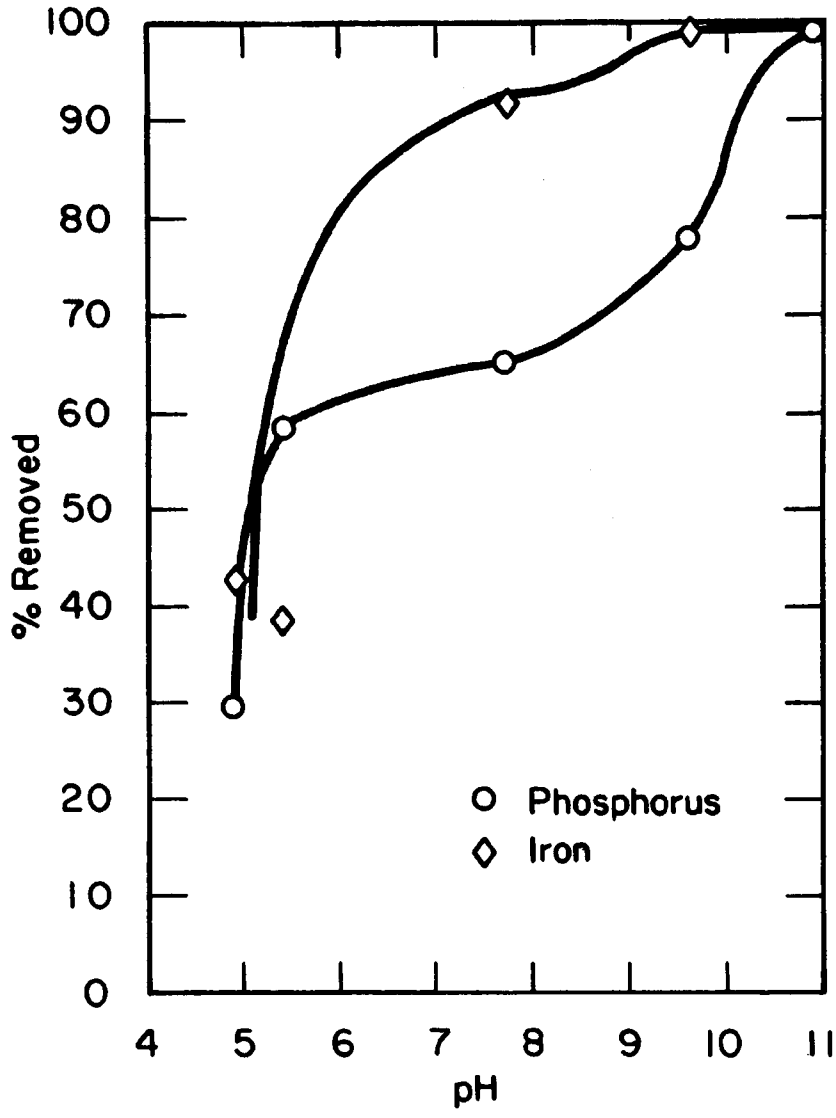


Figure 13. Per cent phosphate (P) and iron (Fe) removal vs pH. pH adjusted before addition of $FeSO_4 \cdot 7H_2O$ with 0.2 normal suspension of $Ca(OH)_2$ Initial phosphate concentration 35.0 mg/L. Mole ratio of Fe:P = 2.0. 5 minutes mixing at 100 RPM, 20 minutes stirring at 20 RPM. 1 hour settling time. Initially solutions saturated with air.

Figures 7, 9, 11, and 13 show an increase of phosphate removal (except Figures 7 and 9 at Fe:P = 9.0) from pH 9.4 and higher, which is attributed to calcium phosphate formation. The changes in calcium concentration were similar to those shown in Table IV.

The results shown in Figure 7 and 9 at Fe:P = 2.0 are explained by the fact that the phosphate removal with ferrous iron is high and no significant improvement may be expected due to calcium phosphate formation.

The oxygen measurements showed a very rapid oxygen decrease in phosphate solution. The oxygen consumption approached in 3 to 4 minutes (at pH = 7.4) the theoretical amount for complete oxygenation of the ferrous compounds. Figure 14 shows the decrease of ferrous iron in the supernatant solution at pH = 7.4. After 1 hour settling time the oxygen concentration in the supernatant solution was 3.4 mg/l and the ferrous iron concentration decreased slowly with time. The total iron and ferrous iron were also determined in the precipitate at pH = 7.4 and Fe:P = 1.5. The ferrous iron in the precipitate after 1.5 hours settling time (precipitate contact time with the solution) was 4.9 percent of the total iron and after 2.5 hours was 2.5 percent. It is apparent that it takes considerable time to oxygenate the last small quantities of ferrous iron in solution and in the precipitate. The reaction rate at constant pH, at least qualitatively, follows the reaction rate found by Stumm (11). It should be mentioned that the phosphate concentration in solution also decreases very rapidly at the beginning and consequently the reaction rate decreases with decreasing phosphate concentration. Chen and Davidson (12) found that the oxygenation rate is second order with respect to phosphate concentration.

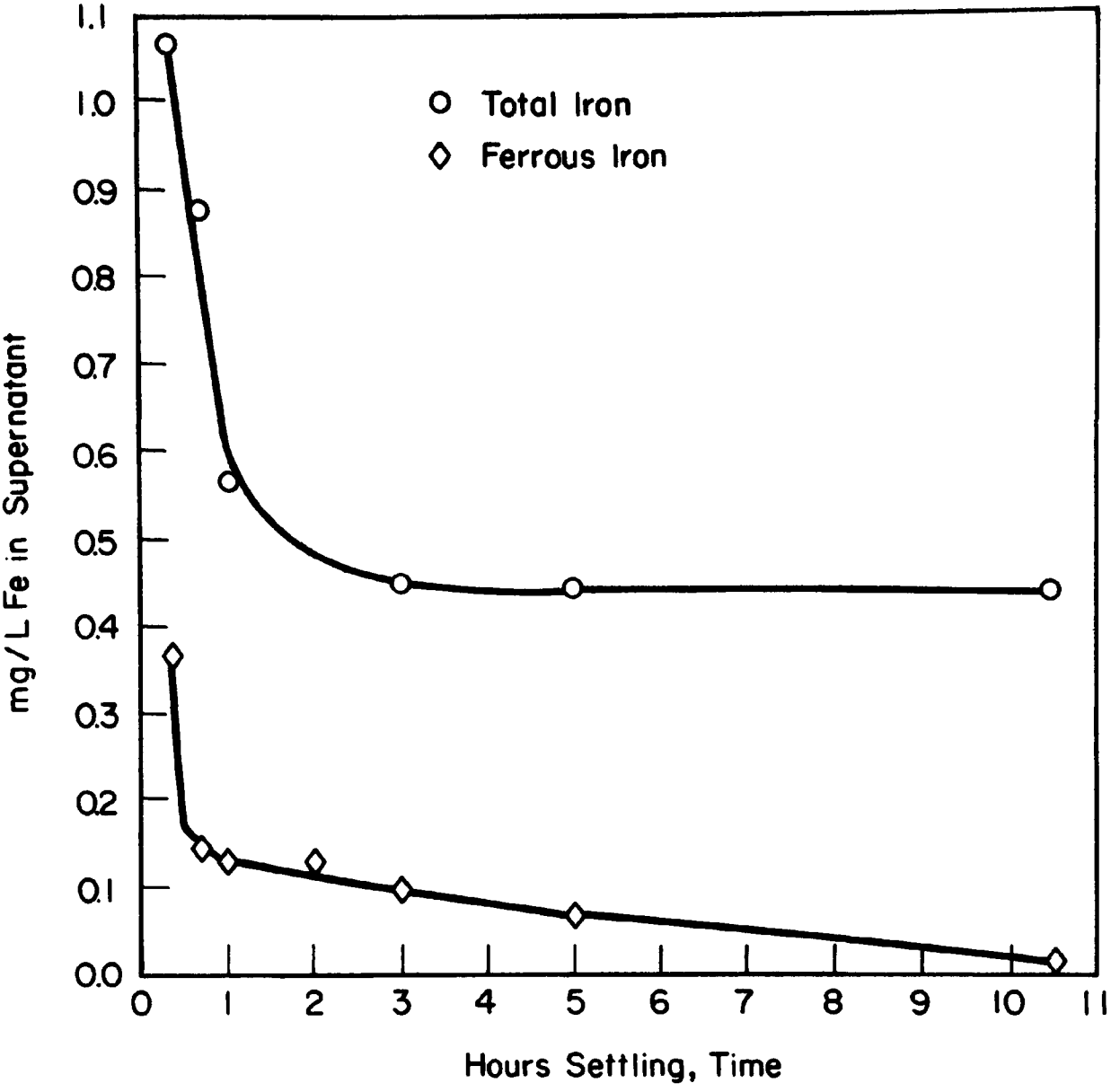


Figure 14. Residual concentration of total iron and ferrous iron vs pH. Initial phosphate concentration 35.0 mg/L PO_4 $FeSO_4$ $7H_2O$ added to mole ratio of Fe:P = 1.5. pH = 7.3 to 7 4 adjusted with 0.2 normal Ca $(OH)_2$ suspension. Initial concentration of O_2 7.8 mg/L.

Figure 15 shows the phosphate removal at different oxygen concentrations in the initial phosphate solution. All three curves show a maximum phosphate removal at the oxygen concentration required for complete ferrous iron oxygenation. The phosphate removal decreases with increasing oxygen concentration above the stocihiometric requirements, showing that the phosphate removal decreases with increasing oxygenation rate of ferrous iron, as indicated by the assumed mechanism.

Figure 16 (curve 2) shows a phosphate removal of 90.3 percent (residual concentration 1.11 mg/l P). Figure 18 (curve 1) shows a phosphate removal of 85.0 percent (residual conc. 1.72 mg/l) when a rapid stream of dispersed air was passed through the solution at the same conditions as Figure 16 (curve 2). The oxygenation rate was higher when passing dispersed air through the solution and consequently a lower phosphate removal was observed. This also is to be expected according to the assumed mechanism.

Figures 7, 9, 11, and 13 show that the phosphate removal is nearly independent of pH in the range of 6.5 to 9.4 when using $Ca(OH)_2$. Figure 20 shows the residual concentration of phosphate and iron when ferric sulfate was used for phosphate removal and pH was adjusted with sodium hydroxide. The same independence of pH in the range of pH from 4 to 8 is observed.

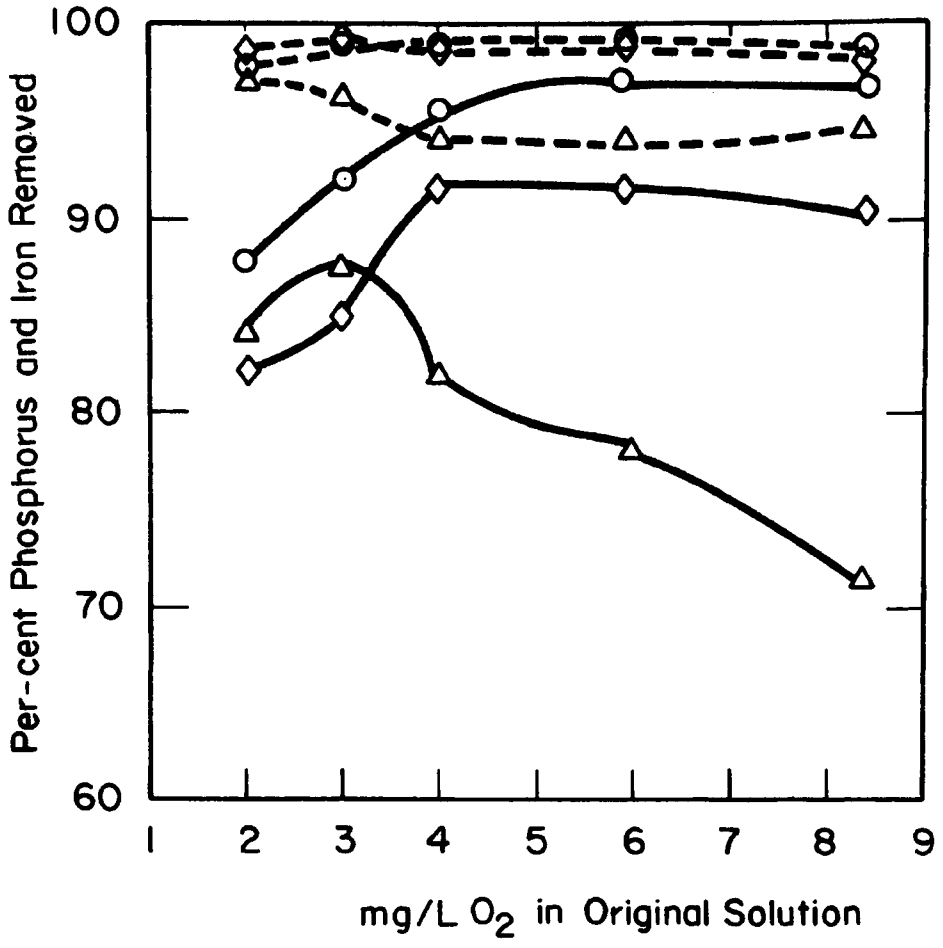
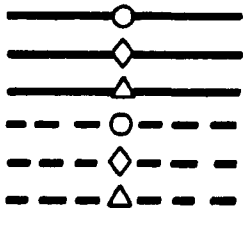


Figure 15. Per cent phosphorus and iron removal vs mg/L O_2 in original solution. pH = 8.0 - 8.5 adjusted with ≈ 0.2 normal $Ca(OH)_2$ suspension. 5 minutes mixing at 100 RPM. 20 minutes stirring at 20 RPM. Settling time 1 hour.



% P removed. PO_4 35.0 mg/L mole ratio Fe:P = 2
% P removed. PO_4 35.0 mg/L mole ratio Fe:P = 1.5
% P removed. PO_4 17.5 mg/L mole ratio Fe:P = 2
% Fe removed. PO_4 35.0 mg/L mole ratio Fe:P = 2
% Fe removed. PO_4 35.0 mg/L mole ratio Fe:P = 1.5
% Fe removed. PO_4 17.5 mg/L mole ratio Fe:P = 2

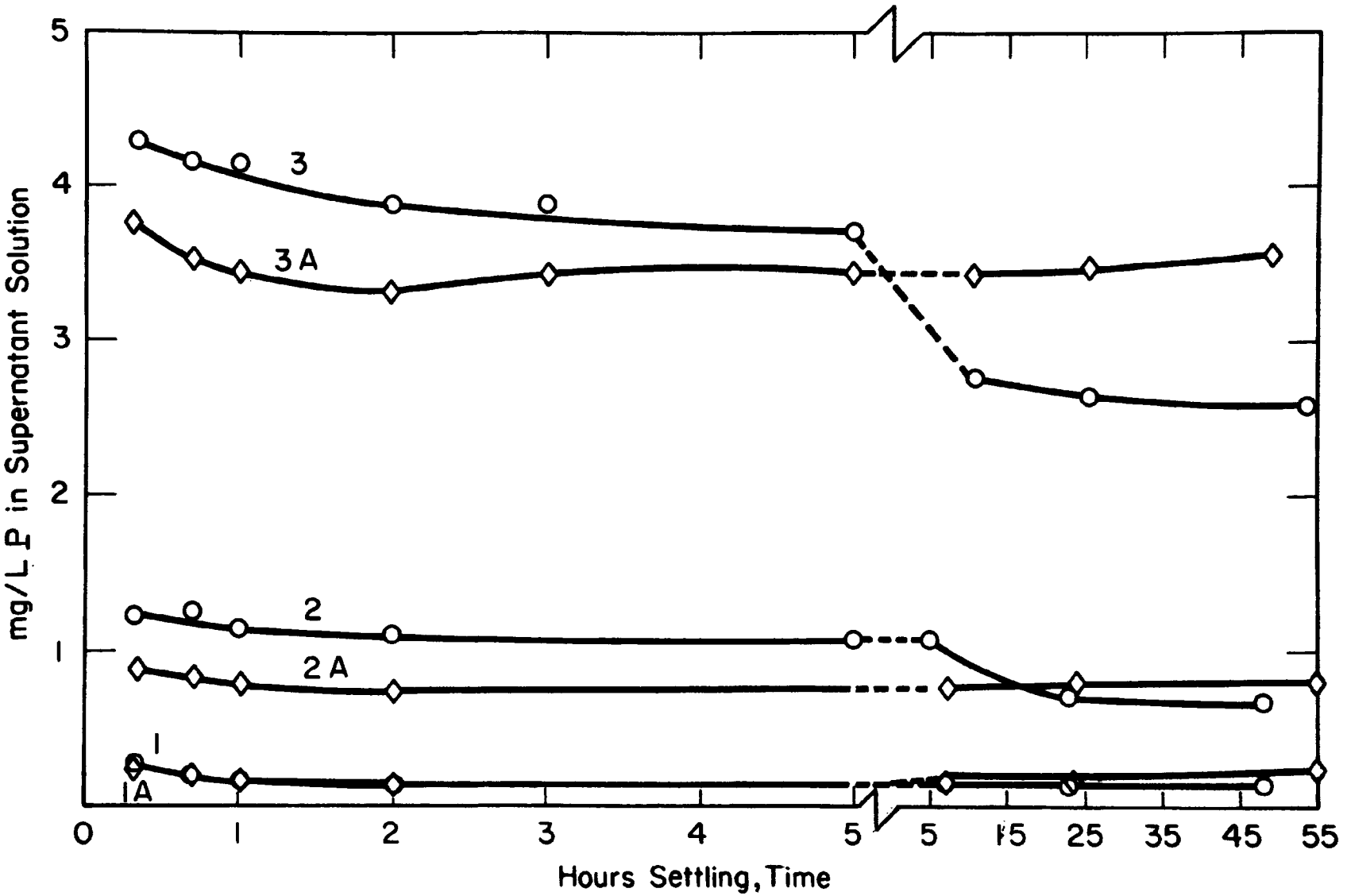


Figure 16. Residual concentration of phosphate (as P) in supernatant solution vs settling time. Initial phosphate concentration 35.0 mg/L PO_4 Solid $FeSO_4$ $7H_2O$ added. pH adjusted with 0.2 normal $Ca(OH)_2$ suspension. pH = 7.0 to 7 4. Initially solutions saturated with air. 5 minutes mixing at 100 RPM, 5 minutes stirring at 20 RPM. Curves 1, 2 and 3 mole ratio Fe:P = 2.0, 1.5, 1.0. Curves 1A, 2A and 3A Fe:P = 2.0, 1.5 and 1.0 plus 1 mg/L A-23.

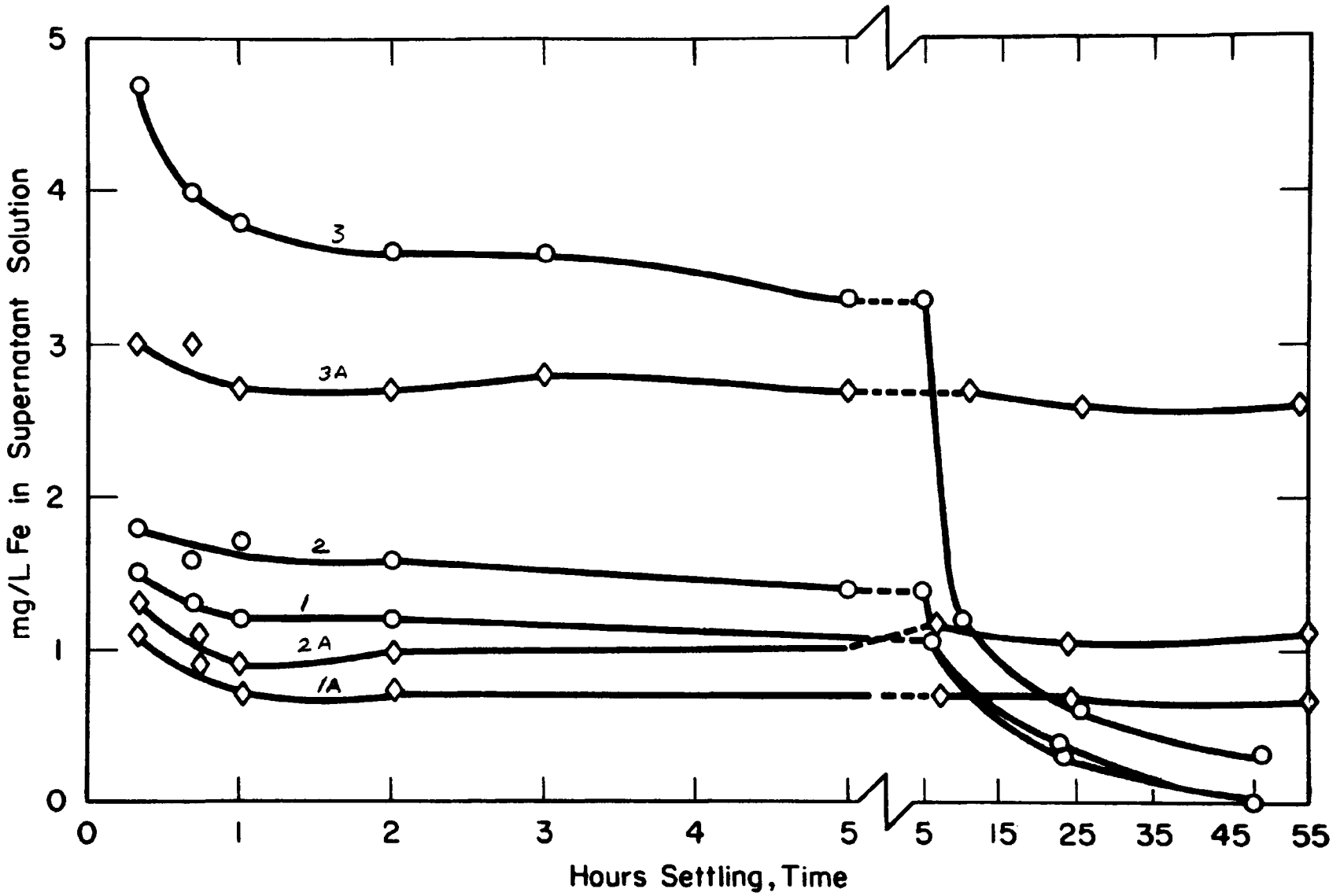


Figure 17. Residual concentration of iron (Fe) in supernatant solution vs settling time. Initial phosphate concentration 35.0 mg/L PO_4 Solid Fe $SO_4 \cdot 7H_2O$ added. pH = 7.0 to 7.4 adjusted with 0.2 normal $Ca(OH)_2$ suspension. Initially solutions saturated with air. 5 minutes mixing at 100 RPM, 5 minutes stirring at 20 RPM. Curves 1, 2 and 3 mole ratio Fe:P = 2.0, 1.5 and 1.0. Curves 1A, 2A and 3A Fe:P = 2.0, 1.5 and 1.0 plus 1 mg/L A-23.

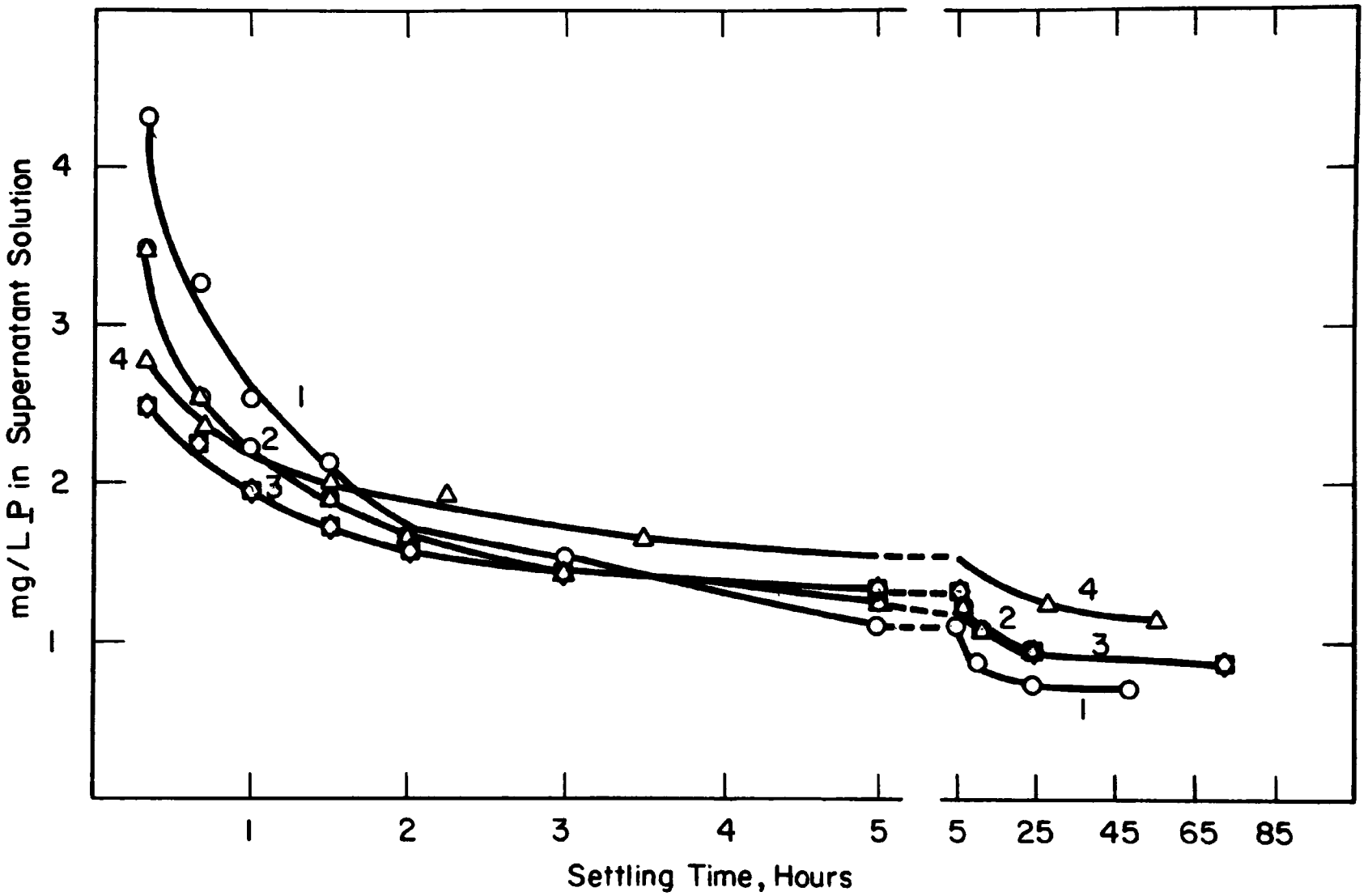


Figure 18. Phosphate in supernatant solution (as P) vs settling time (hours). Dispersed air passed through the solution after addition of Fe SO_4 $7H_2O$ and adjusting the pH. Initial phosphate concentration 35.0 mg/L. Mole ratio Fe:P = 1.5. pH adjusted to 7.3 - 7 4 with 0.2 normal $Ca(OH)_2$ suspension. Curves 2, 3 and 4 added 0.5 mg/L A-23, 1 mg/L A-23, and 1 mg/L A-23 before passing dispersed air through the solution.

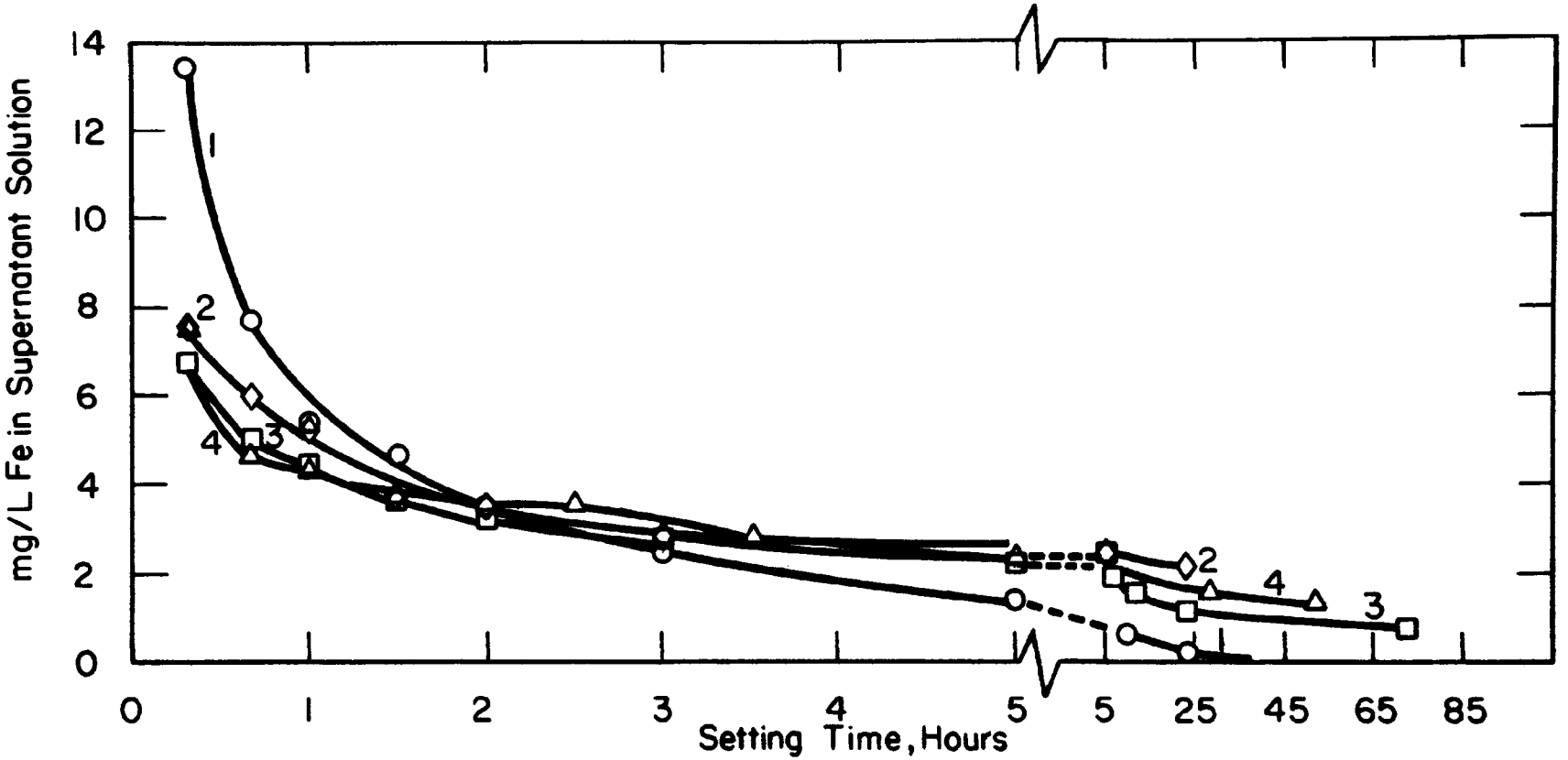


Figure 19. Iron in supernatant solution (as Fe) vs settling time (hours). Dispersed air passed through the solution after addition of $FeSO_4$ $7H_2O$ and adjusting the pH. Initial phosphate concentration 35.0 mg/L PO_4 Mole ratio Fe:P = 1.5. pH adjusted to 7.3 - 7.4 with 0.2 normal $Ca(OH)_2$ suspension. Curves 2, 3 and 4 added 0.5 mg/L A-23, 1 mg/L A-23 and 1 mg/L A-23 before passing air through the solution.

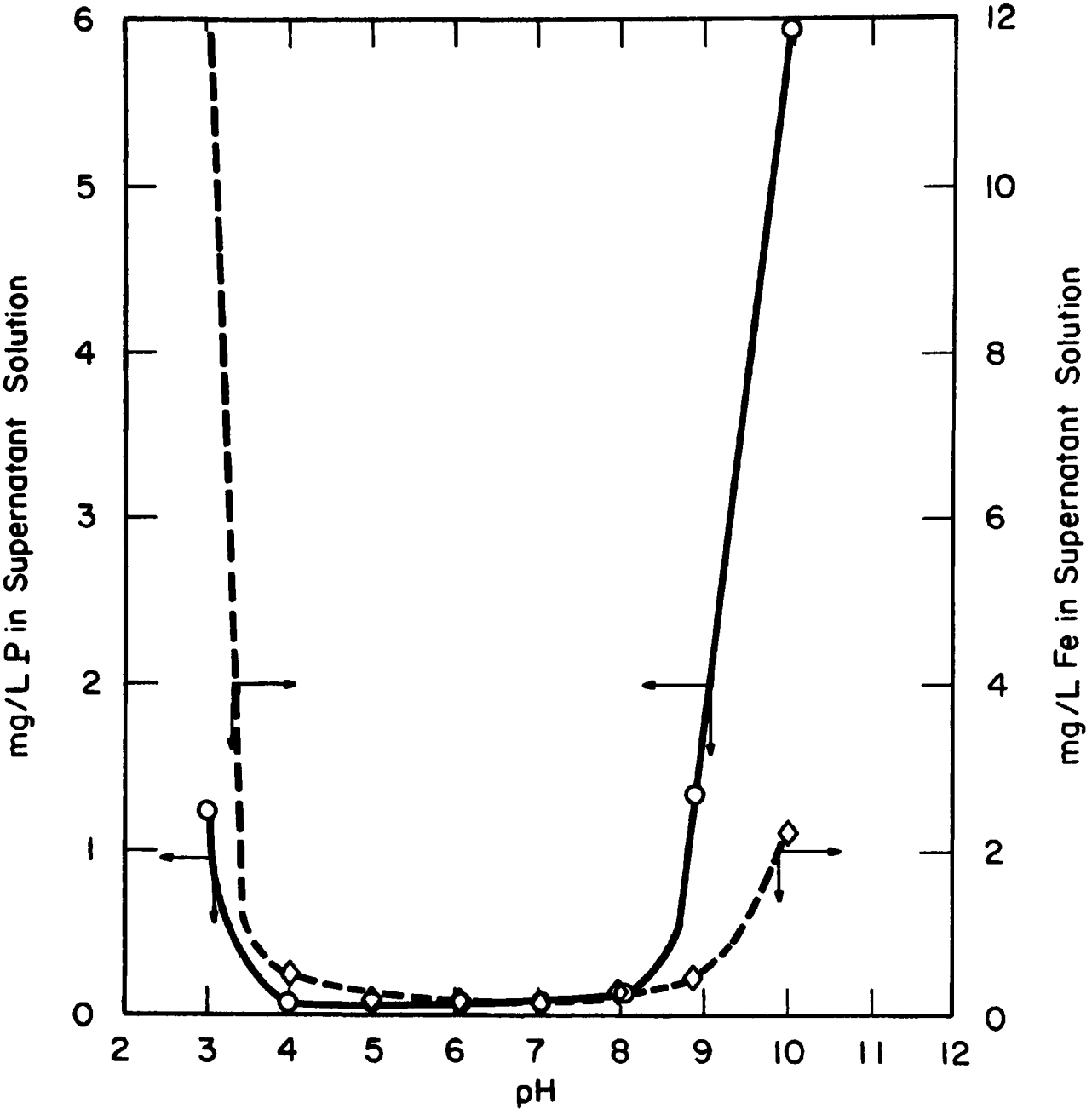


Figure 20. mg/L P and Fe in supernatant solution vs pH. $Fe_2(SO_4)_3$ solution added to mole ratio of Fe:P = 2.0. Initial phosphate concentration 35.0 mg/L PO_4. pH adjusted with 0.2 normal NaOH solution. 5 minutes mixing at 100 RPM, 20 minutes stirring at 20 RPM. 3 hours settling time.

Figure 21 shows the residual concentration of phosphate when the initial phosphate concentration was 105 mg/l (34.3 mg/l)P), pH adjusted to 7.2, and the mole ratio Fe:P = 2.0, 1.5, 1.0, and 0.5. The initial oxygen concentration was 7.8 mg/l. At Fe:P = 2.0, 1.5, and 1.0 the oxygen concentration was lower than required for complete ferrous iron oxygenation. After one hour settling time the phosphate removal was 99.2, 98.0, 91.4, and 53.9 percent at Fe:P = 2.0, 1.5, 1.0, and 0.5, respectively. Figure 16 shows a phosphate removal of 98.6, 89.9, and 63.8 percent at Fe:P = 2.0, 1.5, and 1.0 respectively and initial concentration of phosphate 35.0 mg/l PO_4. The higher phosphate removal at Fe:P = 2.0 and 1.5 and initial phosphate concentration of 105 mg/l PO_4 may be explained by adsorption effects which are not negligible, considering the large quantity of precipitate. The removal at Fe:P = 1.0 is higher than theoretical and can not be explained by the assumed mechanism. There was a striking difference in color of the precipitates at an initial concentration of 105 mg/l PO_4. The precipitate at Fe:P = 2.0 was dark blue and remained blue until it was oxygenated by oxygen absorbed from air. The color then changing to brown. A similar result was obtained at Fe:P = 1.5. At Fe:P = 1.0 the initially dark blue precipitate was quickly oxidized and the color changed to brown. At Fe:P = 0.5 the precipitate was brown. The blue color of the precipitate indicates the formation of ferro-ferric compounds. The phosphate removal should be higher when intermediate ferro-ferric compounds are formed and subsequently oxygenated to ferric phosphate and ferric hydroxide, than when ferrous phosphate is formed and subsequently oxygenated.

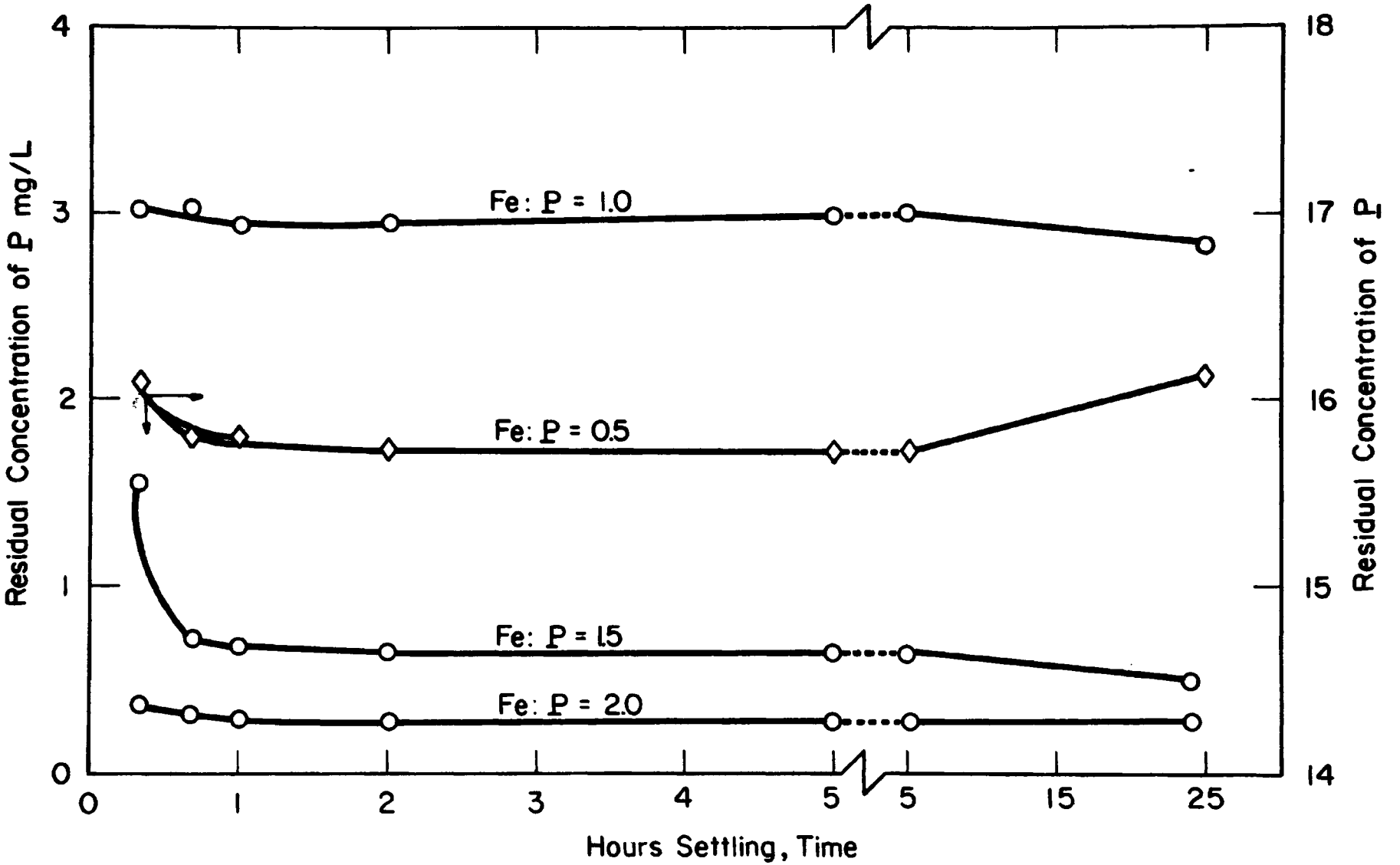


Figure 21. Residual concentration of phosphate (as P) vs settling time (hours). Initial phosphate concentration 105 mg/L PO_4 $FeSO_4$ $7H_2O$ added as solid. pH adjusted with 0.2 normal $Ca(OH)_2$ suspension. 5 minutes mixing at 100 RPM, 5 minutes stirring at 20 RPM. Initially solutions saturated with air.

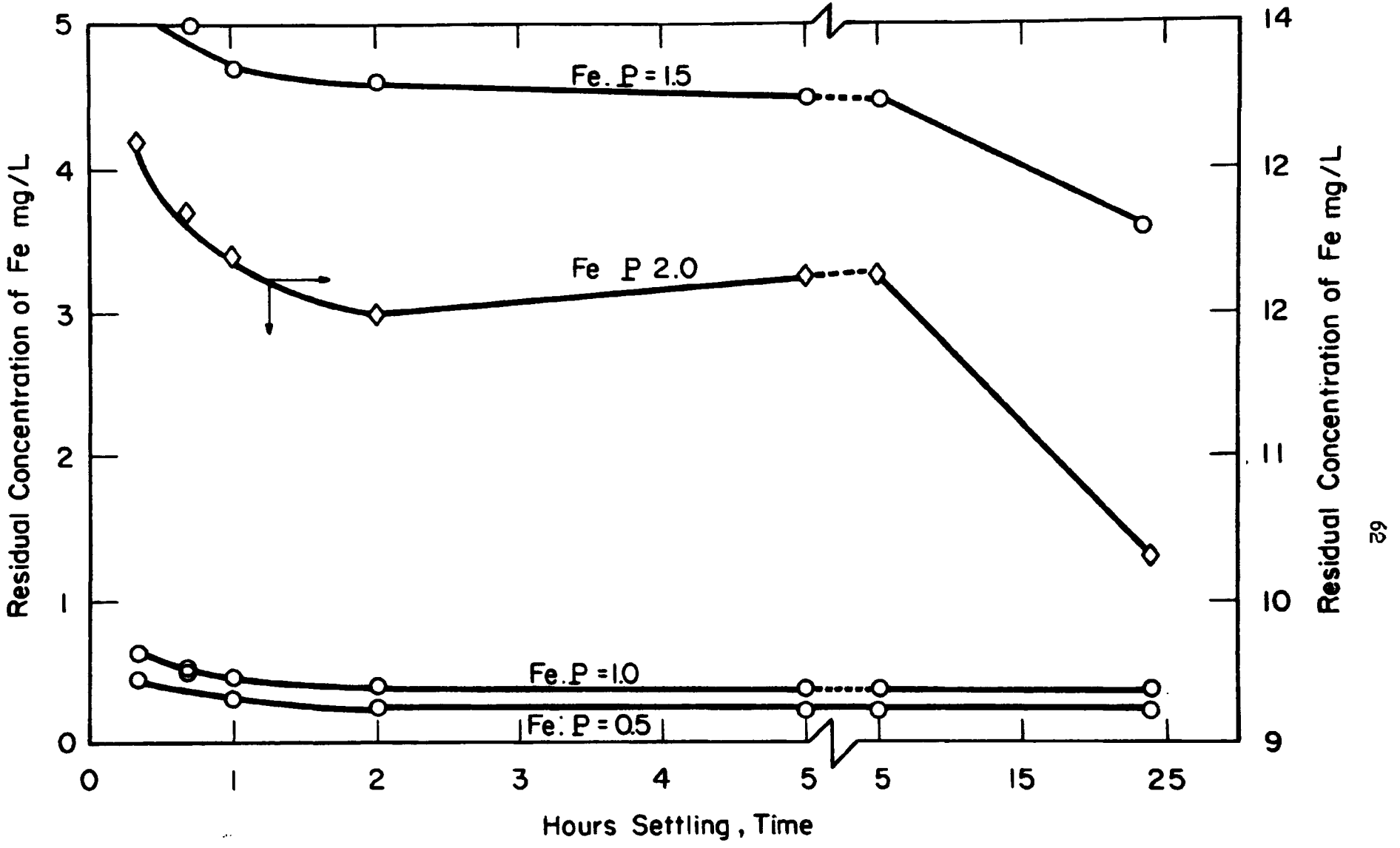


Figure 22. Residual concentration of iron (as Fe) vs settling time (hours). Initial phosphate concentration 105 mg/L. $FeSO_4 \cdot 7H_2O$ added as solid. pH adjusted with 0.2 normal $Ca(OH)_2$ suspension. 5 minutes mixing at 100 RPM, 5 minutes stirring at 20 RPM. Initially solutions saturated with air.

The pH of the 105 mg/l PO_4 solution decreased with time due to oxygenation reaction and hydrolysis of ferric iron and in turn decreased the oxygenation rate. It should be mentioned that using $Ca(OH)_2$ to adjust the pH (to 7 and higher) the concentration of calcium in the solution increases with increasing initial concentration of ferrous sulfate and potassium di-hydrogen phosphate.

The assumed simple mechanism was useful in explaining the results of phosphate removal from phosphate solutions up to 35.0 mg/l PO_4, Fe:P = 2.0, and 8 mg/l O_2. The effects of adsorption and formation of ferro-ferric compounds at higher initial phosphate concentrations limit the range to which the assumed mechanism can be applied to explain experimental results.

Figures 23 and 24 show the moles of phosphate removed per mole of iron, i.e., "the capacity of coagulatant" (2), as a function of residual phosphate concentration. The only difference between those two curves is that the results shown on Figure 23 were taken at an oxygen concentration close to 8 mg/l while the results shown in Figure 24 were obtained by passing dispersed air through the solution. Both curves show a decrease of coagulant capacity with decreasing residual concentrations of phosphate. The curve of Figure 23 shows a change of slope at an iron concentration close to the point where complete oxygenation of ferrous iron by dissolved oxygen is attained. Change of the slope should indicate the change of mechanism and is supported by observation of change in color of the precipitate. The color of the precipitate was brown above the point of change of slope and dark blue below this point.

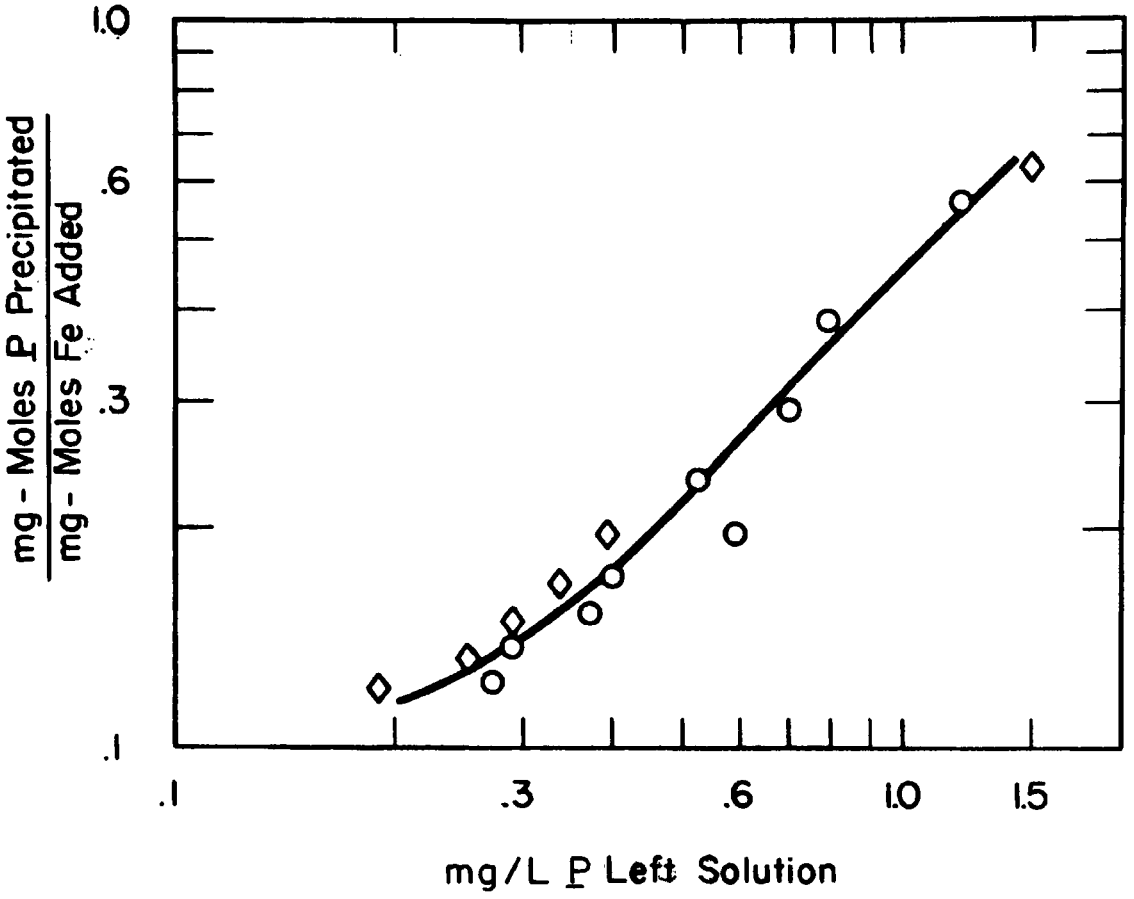


Figure 23. mg-moles phosphate (as P) precipitated per 1 mg-mole iron (Fe) added vs mg/L P left in supernatant solution. Initial concentration of phosphate 35.0 mg/L PO_4 . $FeSO_4 \cdot 7H_2O$ added. pH = 7 1 to 8.1 adjusted with 0.2 normal $Ca(OH)_2$ suspension. Initially solutions saturated with air. 5 minutes mixing at 100 RPM, 20 minutes settling time.

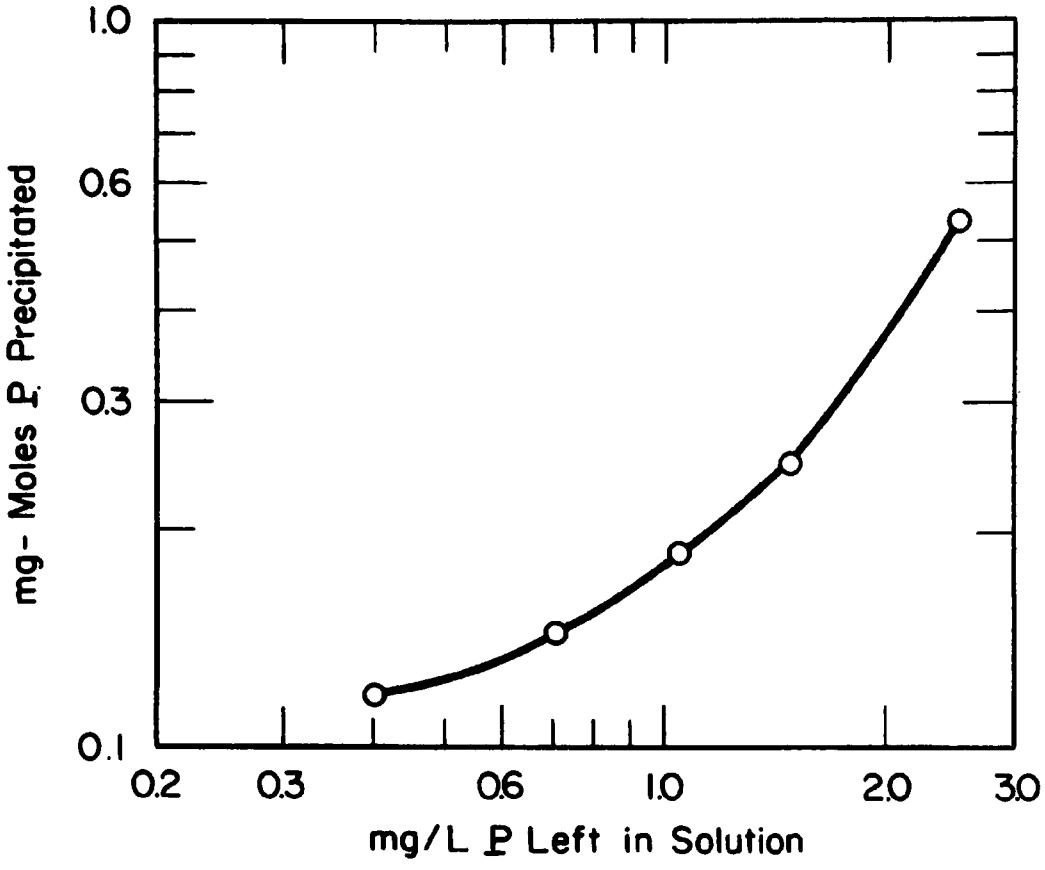


Figure 24. mg-moles phosphate (as P) precipitated per 1 mg-mole Fe added vs mg/L P left in solution. Initial phosphate concentration 35.0 mg/L PO_4 Solid $FeSO_4 \cdot 7H_2O$ added. pH = 7.3 to 7.6 adjusted with 0.2 normal $Ca(OH)_2$ suspension. 5 minutes mixing at 100 RPM, 5 minutes stirring at 20 RPM. 20 minutes settling time. Dispersed air passed through the solution.

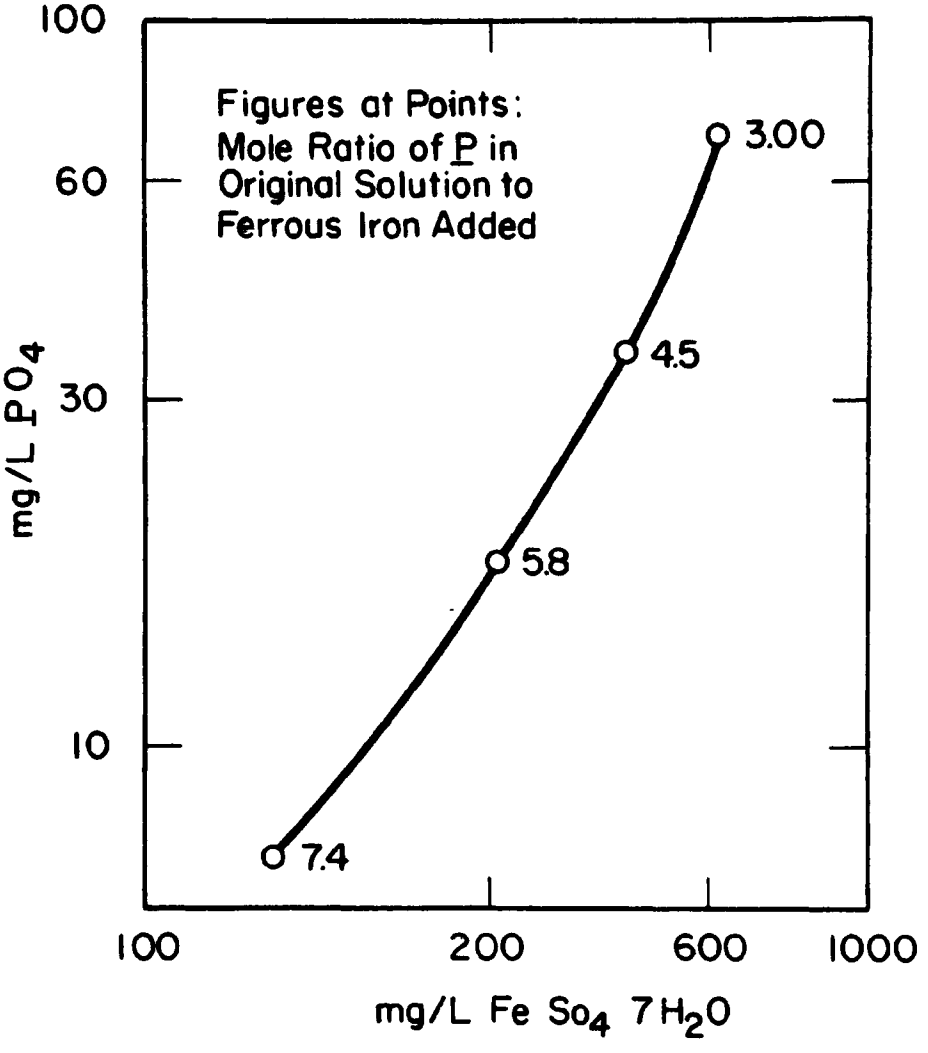


Figure 25. mg/L PO_4 in original solution vs mg/L $FeSO_4 \cdot 7H_2O$ added. pH = 6.5 to 7.0 adjusted with 0.2 normal $Ca(OH)_2$ suspension. 5 minutes mixing at 100 RPM, 5 minutes stirring at 20 RPM. 24 hours settling time. Initially solutions saturated with air.

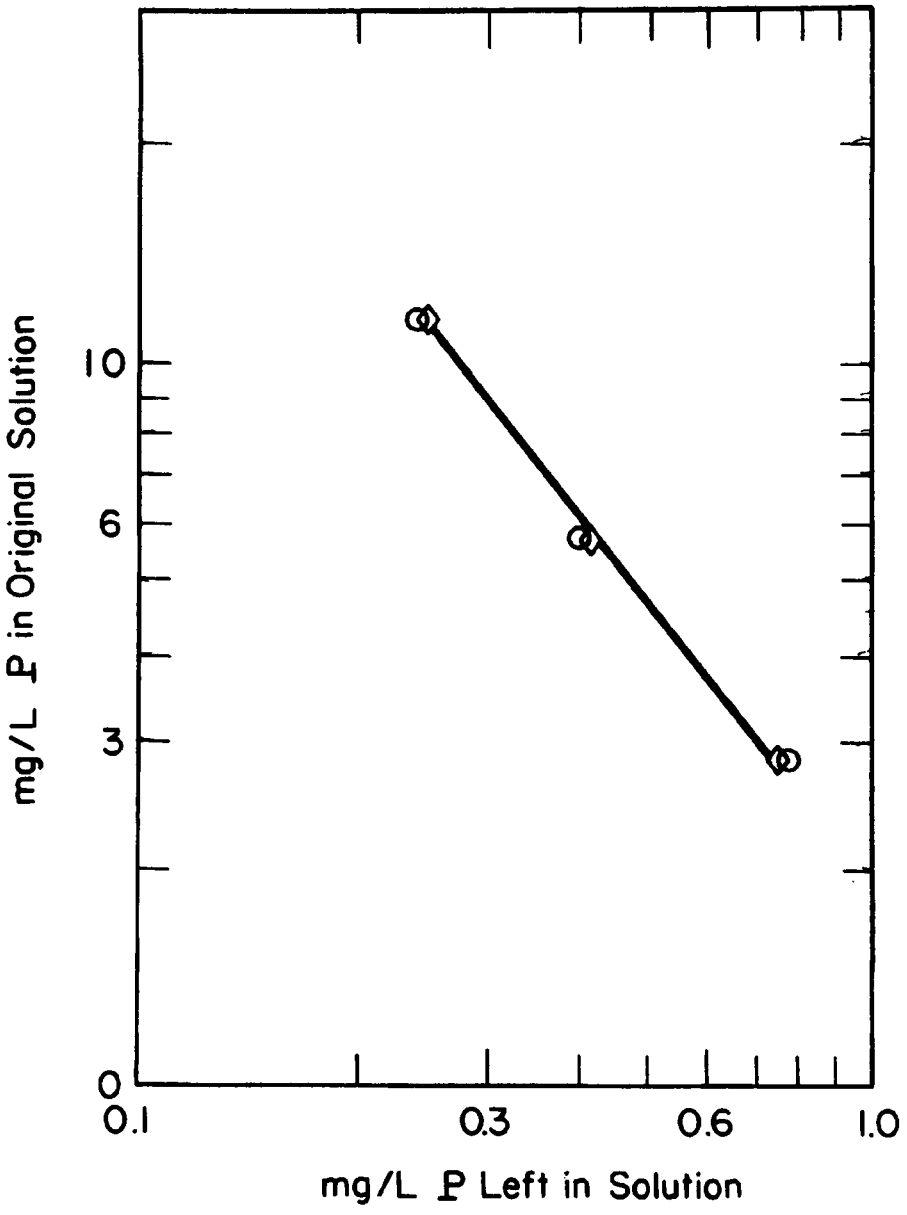


Figure 26. Initial concentration of phosphate mg/L P vs phosphate mg/L P left in solution. Mole ratio of Fe:P = 2.0. $FeSO_4$ $7H_2O$ added as solid. pH = 7.5 to 8.0 adjusted with 0.2 normal $Ca(OH)_2$ suspension. 5 minutes mixing at 100 RPM, 5 minutes stirring at 20 RPM. 1 hour settling time. Initial solutions saturated with air.

Earlier it was pointed out that the assumed mechanism is not valid when formation of ferro-ferric compounds occurs and the change of slope on Figure 23 supports this reasoning. When the residual phosphate concentration shown in Figure 23 and Figure 24 are compared at the same coagulant capacity the residual concentration in Figure 24 is consistently higher, and approximately twice, that of Figure 23. The less efficient phosphate removal, when dispersed air is passed through the solution, is attributed to the higher ferrous iron oxygenation rate. The smooth curves shown Figure 24 indicate a process with overlapping mechanisms which occur over the whole region investigated.

Figure 25 shows the results from Wang's work (9). The plot shows the initial concentration of phosphate in solution vs. the concentration of ferrous iron added to attain "nearly complete phosphate removal" (less than 0.1 mg/l PO_4). The figures at the points are the mole ratios of iron to phosphorus and show that a large excess of ferrous sulfate is required to attain very low residual concentration of phosphate.

Figure 26 shows a plot of mg/l P in original solution vs. mg/l P remaining in supernatant solution at mole ratio of Fe:P = 2.0 and initial concentration of oxygen (8 mg/l), sufficient for complete oxygenation of ferrous iron. The phosphate removal was 98.2, 92.7, and 73.1 percent at the corresponding points shown on the plot. The decrease of phosphate removal with decreasing initial phosphate concentration, i.e., the decrease of phosphate removal with decreasing

initial ferrous iron concentration, is associated with increasing oxygenation rate of ferrous iron. It should be mentioned that the tendency to form colloidal dispersions increased with decreasing initial phosphate concentration. Apparently very small deviations from the adapted precipitation procedure was the cause of change of the colloidal properties of the system. The results shown in Figure 26 are those obtained from runs when the coagulation and flocculation was spontaneous (without detectible transition through colloidal phase).

(2) Effect of Settling Time and Flocculation Aids.

Figure 12 shows the residual concentrations of phosphate as P and iron in the supernatant as a function of settling time when ferric sulfate was used for phosphate removal. From a practical point of view the phosphate removal is nearly complete after one hourssettling time. The iron in the supernatant decreases slowly and approaches very low values with increasing settling time. The pH of the solution also decreases with time and indicates that the decrease of iron is associated with hydrolysis of ferric iron. The ferric hydroxide formed has a tendency to remain in the supernatant solution in very finely dispersed form and the coagulation and flocculation rates were slow.

Figures 16 and 17 (curves 1, 2, and 3) show the remaining phosphate as P and iron in the supernatant as a function of settling time when ferrous sulfate was used for phosphate removal. The curves follow the same pattern as in Figure 12 but the phosphate remaining in the supernatant was higher and the phosphate decrease with time was also higher. The presence of a larger fraction of finely dispersed ferric phosphate may account for the decrease of phosphate in the supernatant with time. The curves 1, 2, and 3 show an iron concentration of 0.03, 0.03, and 0.3 mg/l respectively after 48 hours settling.

Figures 18 and 19 (curves 1) show the decrease of phosphate and iron in supernatant with time when ferrous sulfate was used for phosphate removal and dispersed air was passed through the solution. The suspended flocs were small and settled much slower during the first 2 hours as compared to the results shown by curves 2 of Figures 16 and 17. After two hours of settling the curves follow a similar pattern as the curves shown in Figures 16 and 17, except that phosphate removal was lower.

Figures 21 and 22 show the phosphate and iron remaining in the supernatant as a function of settling time when ferrous sulfate was used for phosphate removal and the initial concentration of phosphate was 105 mg/l PO_4. The curves of phosphate remaining in the supernatant are similar to those shown in Figure 16 except that the concentration of phosphate remaining in the supernatant is higher and the decrease of phosphate with settling time is less pronounced. The concentration of total iron in the supernatant was high at Fe:P = 2.0 and 1.5 because of higher solubility of ferrous iron which was still present after 25 hours of settling.

Curves 1A, 2A, and 3A, in Figures 16 and 17 and curves 2, 3, and 4 in Figures 18 and 19 show the result obtained when Purifloc A-23, a high molecular weight anionic polyelectrolyte manufactured by Dow Chemical Company, was added to the suspension. In the presence of A-23 the coagulation, flocculation, and sedimentation properties of the system were greatly improved. In 6 to 7 minutes the solids were settled and the supernatant was clear. After longer settling times the

residual concentration of phosphate and iron in the supernatant was higher with A-23 compared to the results obtained without addition of A-23. The A-23 showed a tendency to stabilize the colloidal dispersi at low phosphate and iron concentrations. The stabilizing effect of A-23 on colloidal dispersion shows that the A-23 was not added at the optimal conditions. More work is required to arrive at the optimal conditions necessary for efficient use of the polyelectrolyte.

3. Effect of CO_2 and $Ca(OH)_2$ Requirements.

Phosphate was precipitated with ferrous sulfate by adjusting the pH with $Ca(OH)_2$ suspension from solutions containing known concentrations of dissolved CO_2. The mole ratio of Fe:P was 2.0 and the pH was adjusted to 8.0. Compared to runs made in the absence of CO_2, no decrease of phosphate removal was observed with CO_2 up to 20 mg/l. At higher CO_2 concentrations a decrease of phosphate in the supernatant was observed and was attributed to the formation of calcium phosphate and/or adsorption of phosphate on the precipitated calcium carbonates. The amount of $Ca(OH)_2$ to arrive at pH = 8.0 increased with increasing CO_2 concentration. The phosphate-ferrous sulfate solution was also titrated with 0.04 normal $Ca(OH)_2$ solution. The titration curves, pH vs ml $Ca(OH)_2$ solution, showed the maximum pH change at pH = 8.0. With increasing CO_2 content the general shape of the curves remained the same but the curves were shifted toward increasing ml of $Ca(OH)_2$ solution. For example: to arrive at pH = 8.0 in CO_2 free solution, 28.0 mg/l CaO were required compared to 29.6 mg/l required for solution containing 17 mg/l CO_2.

To illustrate the quantity of $Ca(OH)_2$ used in the runs described above the following example is given: To adjust the pH to 8.0 at initial PO_4 concentration of 35.0 mg/l and mole ratio of iron to phospherous of 2.0, 1.5, and 1.0; 28.0, 22.4, and 16.8 mg/l as CaO were added in absence of CO_2. The quantities of $Ca(OH)_2$ required increased with increasing initial concentration of KH_2PO_4, $FeSO_4 \cdot 7H_2O$ and increasing pH.

4. Settled Precipitate Volume.

For runs in which the volume of precipitate were examined, the precipitation of phosphate with ferrous sulfate was conducted according to the adopted procedure given on page 38, but after 20 minutes of stirring at 20 RPM the suspension (800 ml) was poured in 1000 ml graduate cylinders and the volume of settled precipitate was measured after one hour settling time. The average volumes of precipitates at initial PO_4 of 35.0 mg/l and Fe:P = 2.0, 1.5, and 1.0 were 30, 24, and 17 ml respectively or 3.7, 3.0 and 2.1 percent of total solution volume. The precipitate volumes after one hour settling time were nearly proportional to the ferrous sulfate added.

5. Titration Curves

Figure 27 shows the titration curves of solutions with 0.0433 normal $Ca(OH)_2$ solution. Curves II and IV were obtained by using oxygen free solutions and exclusion of oxygen during the titration.

The composition of the solutions titrated and the pH at which precipitate formed were as follows:

Curve I: 1.000 mg-equivalent H_2SO_4 in 600 ml H_2O

Curve II: 1.000 mg-equivalent H_2SO_4 and 0.441 mg-moles $FeSO_4 \cdot 7H_2O$ in 600 ml H_2O. Precipitate of ferrous hydroxide appears at pH = 8.7.

Curve III: 1.000 mg-equivalent H_2SO_4 and 0.221 mg-moles of KH_2PO_4 in 600 ml H_2O. Precipitate of calcium phosphate formed at pH = 8.5.

Curve IV: 1.000 mg-equivalent H_2SO_4, 0.221 mg-moles KH_2PO_4, and 0.441 mg-moles $FeSO_4 \cdot 7H_2O$ in 600 ml H_2O. Ferrous phosphate precipitate appears at pH = 6.8 and ferrous hydroxide at pH = 9.4.

Curve V: 1.000 mg-equivalents H_2SO_4, 0.441 mg-moles $FeSO_4 \cdot 7H_2O$, 0.221 mg-moles KH_2PO_4, and 0.3 mg-moles dissolved O_2 in 600 ml H_2O. Ferric phosphate precipitate appeared at pH = 3.6.

Curve VI: 1.000 mg-equivalent H_2SO_4 and 0.441 mg-moles ferric iron added as $Fe_2(SO_4)$ in 600 ml water. Ferric hydroxide formed below pH = 2.6.

Curve VII: 1.000 mg-equivalent H_2SO_4, 0.221 mg-moles KH_2PO_4, and 0.441 mg-moles ferric iron added as $Fe_2(SO_4)_3$. Ferric phosphate and ferric hydroxide precipitate formed below pH = 2.4.

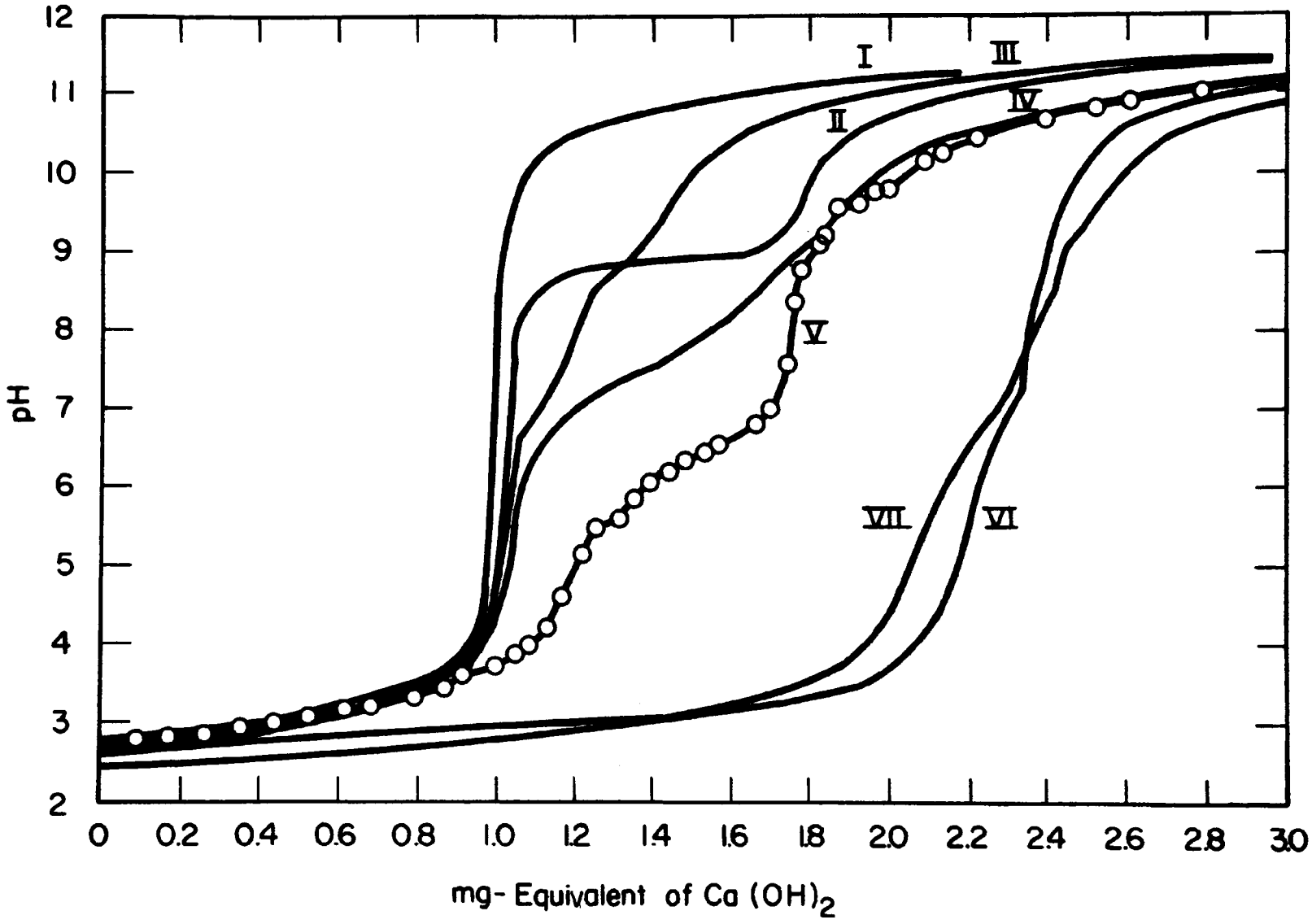


Figure 27. Titration Curves: pH vs mg-equivalents of $Ca(OH)_2$

TABLE V.* REMOVAL OF PYROPHOSPHATE AND ORTHOPHOSPHATE WITH $FeSO_4 \cdot 7H_2O$

Initial phosphate solution: 11.43 mg/l P as $Na_4P_2O_7$ and 11.43 mg/l P as KH_2PO_4

pH adjusted with 0.2 normal $Ca(OH)_2$ suspension

5 minutes mixing at 100 RPM, 20 minutes stirring at 20 RPM; settling time 1 hour, then filtered (Whatman #43), all solutions initially saturated with air

$FeSO_4 \cdot 7H_2O$ Added mg/l	Mole ratio Fe:P	pH	Supernatant Solution mg/l P			Percent P Removed		
			ortho	pyro	total	ortho	pyro	total
770	3.7	8.3	0.25	0.02	0.27	97.8	99.8	98.8
610	3.0	7.2	0.07	0.09	0.16	99.4	99.2	99.3
460	2.2	7.9	0.75	0.23	0.98	93.4	97.4	95.7

*Chun-jen Wang (9)

TABLE VI. REMOVAL OF TRIPHOSPHATE AND ORTHOPHOSPHATE WITH $FeSO_4 \cdot 7H_2O$

Initial phosphate solution: 5.71 mg/l P as KH_2PO_4
pH adjusted with 0.2 normal $Ca(OH)_2$ suspension
5 minutes mixing at 100 RPM. 20 minutes stirring at 20 RPM; settling time 1 hour

$FeSO_4 \cdot 7H_2O$ mg/l	Mole Ratio Fe:P	pH	Supernatant Solution mg/l P			Percent P Removed		
			ortho	tri	total	ortho	tri	total
308	3.0	7.3	0.34	0.04	0.38	94.1	99.3	96.7
206	2.0	7.3	0.44	0.04	0.48	92.3	99.3	95.8
154	1.5	7.3	0.54	0.18	0.72	90.5	96.8	93.7
103	1.0	7.4	2.60	1.50	4.10	54.5	73.7	64.1

6. Removal of Polyphosphates.

The experimental procedure described on page 38 was followed except for phosphate determination in supernatant. The total phosphate and the polyphosphate was determined by the procedure given in Standard Methods for the Examiniation of Water and Wastewater, Twelfth Edition, 1965, pp. 234-238.

At relatively high initial pyrophosphate concentrations, Table V, the phosphate precipitates coagulated and settled slowly. The results shown on Table V were obtained on filtered supernatant. Triphosphate, Table VI, up to a concentration of 5.7 mg/l did not affect the coagulation and settling properties of the system. The pyrophosphate and the triphosphate removal was higher than for orthophosphate. On the average the removal of total phosphate was lower by approximately two percent compared to phosphate removal from pure orthophosphate solution at the mole ratio of iron to phosphorus of 2.0 and lower.

7. Flow Process.

A continuous flow equipment was constructed and operated. The construction materials were "Plexiglass" and "Pyrex". The description of equipment, operation and some results are found in Wang's M.S. thesis (9). Difficulties were encountered in the operation of sedimentation tanks. The coagulation, flocculation and settling of the solids was slower than in the batch process. When the effluent from the settling tank was allowed to settle at quiescent conditions the phosphate removal was similar to the batch process provided the initial phosphate and oxygen concentration, mole ratio of iron to phosphorus, and the final pH of the solution, were similar.

8. Conclusions.

(1) Phosphate removal was primarily determined by the mole ratio of iron to phosphate. The phosphate removal increased with increasing iron to phosphate ratio, and decreased rapidly below a mole ratio of iron to phosphate of 1.5. Phosphate removal also decreased with decreasing initial concentration of phosphate. Up to 98 percent and up to 91 percent phosphate removal was attained at the mole ratio of iron to phosphorus of 2.0 and 1.5 respectively at initial concentration of 35.0 mg/l PO_4 and the residual concentration in the supernatant was 0.16 to 0.21 mg/l P and 0.7 to 0.8 mg/l P respectively. Economical considerations suggest a mole ratio between 1.5 and 2.0.

(2) Phosphate removal was independent of pH in the range 7 to 9, using calcium hydroxide for pH adjustment. Above a pH of 9 phosphate was also precipitated as calcium phosphate.

(3) Dissolved oxygen affected the phosphate removal. Higher phosphate removal was attained when dissolved oxygen was present in an amount just sufficient for complete oxygenation of ferrous iron. The phosphate removal was higher (98 and 91 percent) when dissolved oxygen was present compared to phosphate removal (89 and 85 percent) from oxygen-free solutions at mole ratio of iron to phosphorus of 2.0 and 1.5 respectively and initial concentration of phosphates 35.0 mg/l PO_4.

(4) A mechanism of the process was proposed to explain the experimental results of phosphate removal with ferrous sulfate from solutions containing dissolved oxygen. The validity of the assumptions used in the proposed mechanism were verified by the experimental results provided that sufficient dissolved oxygen was present for complete oxygenation of ferrous iron.

(5) The residual concentration of iron in supernatant solution (0.6 to 0.8 mg/l) was lower in solutions containing dissolved oxygen sufficient for complete oxygenation of ferrous iron compared to residual concentration of iron in oxygen-free solutions.

(6) From a practical point of view, the settling of insolubilized phosphate was complete after one hour, using calcium hydroxide for pH adjustment. The residual concentration of iron in the supernatant solution after one hour settling time was 1.0 to 1.5 mg/l and up to 48 hours of settling was required to attain residual iron concentrations below 0.1 mg/l Fe. The tendency of the insolubilized phosphates and iron compounds to form colloidal dispersions increased with decreasing initial phosphate concentration (below 35.0 mg/l PO_4) and consequently affected the phosphate removal.

(7) The presence of carbon dioxide up to 20 mg/l did not affect the phosphate removal. The consumption of calcium hydroxide for pH adjustment increased with increasing carbon dioxide concentration.

(8) Higher pyrophosphate and triphosphate removal was observed compared to orthophosphate removal from solutions containing equal amounts (as phosphorus) of polyphosphate and orthophosphate. However, the total phosphate removal from 1:1 mixtures of ortho and polyphosphate was slightly less (approximately 2 percent) than the total phosphate removal from pure orthophosphate solutions.

SECTION 7

THE REMOVAL OF PHOSPHATE PRECIPITATES BY FLOTATION

The work described below was done to evaluate the potential application of flotation techniques to the separation of phosphate precipitates. Both Microflotation and dissolved air flotation were investigated in this regard. For clarity, procedures and results for the two techniques are presented and discussed separately. The discussions of the chemistry of phosphate precipitation presented in the previous sections of this report apply to the work presented herein, but will not be reiterated in detail.

Microflotation

Microflotation is a relatively new technique, in which flotation of an insoluble floc is enhanced by the addition of a collector or surface active agent. The collector absorbs both on the floc particles and on the gas bubbles. Rising gas bubbles carry the precipitate to the surface and form a foam which is removed and collapsed. Microflotation differs from conventional froth flotation in that a frother (e.g., ethyl alcohol) is added to the system to reduce the bubble size. This allows the operation of the system at very low gas flow rates. Using the technique of microflotation, it is often possible to remove a high percentage of precipitated material within a few minutes, whereas conventional settling and filtration would normally require several hours for an equivalent removal. Descriptions and applications of microflotation have been reported by Rubin, et al, (14, 15, 16) and by Rubin (17).

Figure (28) shows the basic apparatus design, which is similar to the system developed by Rubin (18, 19, 15). The essential characteristics of the system consist of a gas source equipped with a precise flow rate control and connected to a flotation cell. The cell used in this study consisted on a 600 ml glass Buchner funnel having a 10 cm diameter, and fitted with a fine sintered glass frit with pore sizes from 4.0 to 5.5 microns, which acted as a gas diffusor plate.

In the studies described below, iron salts were used to precipitate phosphate from the solutions tested. The general operating procedure was to place 360 ml of distilled water in the flotation cell, and adjust the gas flow rate to 20 ml/min. After gas flow was initiated, the pertinent reagents were added in the following sequence; (a) phosphate solution, (b) iron solution, (c) base for pH adjustment, and (d) distilled water to bring the total volume to 400 ml. Following reagent addition, the system ions allowed to reach pH equilibrium ($\approx$ 5 min.), and an additional 10 minutes was allowed for flocculation. Then, the collector-frother solution was added, and the sampling schedule began. All samples were taken in pairs, one being analyzed for phosphate, and the other for iron. A Sargent pH meter equipped with a glass electrode was used for pH measurements, and where applicable, a Yellow Springs Instrument Co. Model 51 oxygen meter was used for dissolved oxygen measurements.

Reagents

The phosphate make-up solution contains 2,0062 gm. per liter of reagent grade KH_2PO_4. 10 ml. of this reagent in a 400 ml solution will produce 35 ppm phosphate (PO_4).

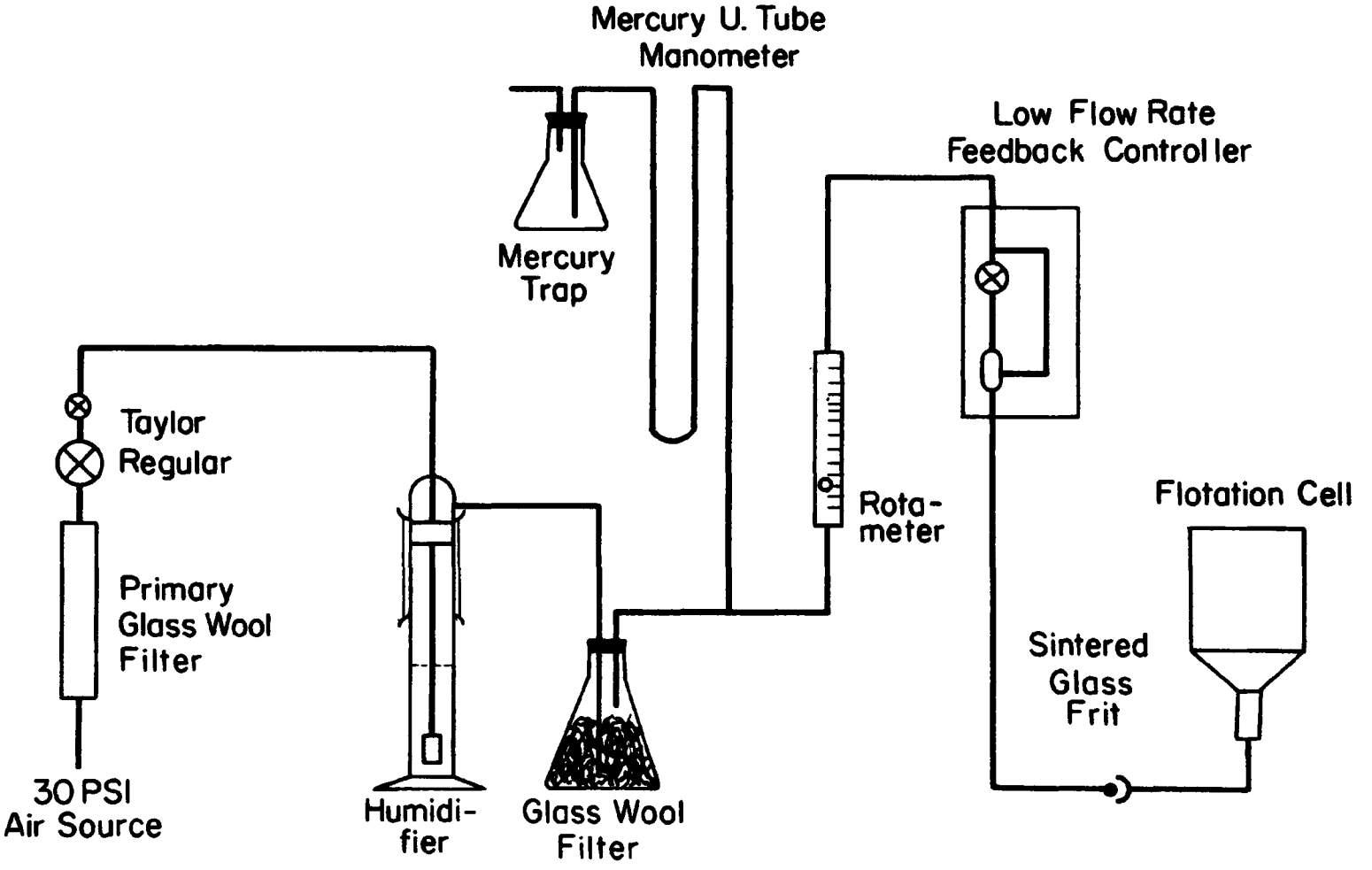


Figure 28. Microflotation system.

Ferric sulfate make-up solution is obtained by adding 5.8929 gm. of ferric sulfate to a solution containing 2.75 ml of concentrated sulfuric acid and 100 ml. of distilled water and diluting to one liter. 10 ml. of this reagent in a 400 ml. solution produces 41.17 ppm. Iron (III) ions or a molar ratio of 2:1, iron(III) to phosphate when combined with the phosphate reagent.

Ferrous sulfate make-up solution is made by adding 50 gm. of KH_2SO_4 to about 200 ml of boiled double distilled water. Following the dissolving of 8.1847 gms of reagent grade ferrous sulfate, the solution is diluted to one liter with boiled double distilled water. The make-up solution yields 41.17 ppm iron(II) ions for a molar ratio of 2:1, iron(II) to phosphate when added with 10 ml of the phosphate reagent to a 400 ml solution.

The pH adjustor is either a 0.2 N solution of sodium hydroxide for Systems I, II and III or a 0.2 N suspension of calcium hydroxide for Systems IV and V.

Except for part of System IV, the collector and frother were combined and added together with a syringe. One liter of Ctab (hexadecyl-tri-methyl ammonium bromide) make-up solution contained 0.8000 gm of Ctab and 50 ml of 95 percent ethyl alcohol. A 10 ml shot of this reagent to a total of 400 ml of solution yields 20 ppm. Ctab and 0.5 ml of ethanol. One liter of NaLS (sodium lauryl sulfate) obtained from Proctor and Gamble, make-up solution contained 0.6330 gm of NaLS and 50 ml. of ethyl alcohol. 10 ml. of the NaLS make-up in a 400 ml solution will produce 15.82 ppm. NaLS and 0.5 ml of ethanol. For studying the effect of surfactant concentration in System IV, the same concentrations of collector make-up solutions were prepared without the alcohol. The

collector was added in 12.5 ml, 2.5 ml, 5 ml, 2 ml, or 1 ml. injections while 0.5 ml of the ethanol frother was being simultaneously injected.

Analysis

Determination of phosphate was made by the Molybdenum Blue - Hydrazine Sulfate Photometric Method adapted for water analysis from the 1964 Book of A.S.T.M. Standards, Part 31, Chemical Analysis of Metals, pp. 97-100. This method of analysis was chosen because it offers the least interference from iron.

Iron analyses were made by the Phenanthroline Photometric Method adapted for water analysis from Standard Methods, Twelfth Edition (1965), prepared and published by the American Health Association.

The photometric analyses were made on a Beckman Spectrophotometer Model DU, using 1 cm. and 5 cm cells.

Results

Before going into a detailed discussion of the results, the mechanism of precipitate flotation will be briefly reviewed. The collector, a surface active agent used to float hydrophilic particles, has a dual purpose; adsorption on the air bubble, and adsorption on the particle. To accomplish the two-fold responsibility, the collectors used in this study are composed of two functional groups, the charged or ionized part, and the hydrophobic part. The hydrophobic end is usually a long chain hydrocarbon, as in the case of Ctab and NaLS. The hydrophobic part adsorbs at the interface between the fluid and the bubble.

The charged end of the collector adsorbs on the floc particle. In precipitate flotation a large floc particle containing millions of precipitated molecules can be made floatable by the adsorption of a monolayer of collector ions. For this condition, less than stoichiometric portions of collector are required.

Simply, the collector acts as a bridge between the floc particle, which has adsorbed the ionic end of the collector and the air bubble liquid interface which has adsorbed the hydrophobic end. The change in density resulting from the connection of the floc with the bubble causes the particle to rise to the surface where it is held in the foam phase.

One of the factors that influences the efficiency of the flotation system is the number of collisions between the bubbles and the floc particles. Removal efficiency is also dependent upon the orientation of the collector at collision. In this study the gas flow rate and the frother concentration were held constant. This implies that the number of bubbles produced should be relatively constant. Since the thickness of the foam did not seem to vary for changes in pH and phosphate removal, it appears that collector adsorption on the bubble is also a constant. For these reasons it is assumed that floc removal is independent of collector adsorption on the bubbles and is limited by adsorption of the collector on the floc.

In this study a frother, ethyl alcohol, was added simultaneously with the collector. The alcohol was observed to reduce the bubble size enormously. Although the reduction of bubble size greatly increased the adsorption interface area, no evidence was obtained to support any additional functions of the alcohol.

The data presented below are drawn from raw data plots of the type shown in Figure 29, which is typical of the experimental runs with regard to the time required for iron and phosphate removals to approach a constant value, after addition of the collector-frother. Since equilibrium was reached in all cases within 30 minutes, the 30 minute data are used in the presentations to follow. Data for the five systems studied will be presented separately. The figures presented here are intended only to identify the conditions required for effective phosphate and iron removal, with pH, choice and concentration of coagulant, choice of collector, and availability of dissolved oxygen being the major process variables. For a discussion of the results in terms of the fundamental chemical considerations involved, the reader is referred to Barrick (20)

(a) System I

In this system, ferric sulfate was used as the coagulant, nitrogen as the gas phase, and sodium hydroxide for pH adjustment. Both Ctab and NaLS were employed as collectors. Quantitatively, the system components were:

KH_2PO_4	35 ppm as PO_4
$Fe_2(SO_4)_3$	as required to give the desired P:Fe molar ratio
NaOH	as required
N_2	20 ml/min

The process results obtained when using 20 ppm of Ctab as a collector, 0.5 ml C_2H_5OH as a frother, and a P:Fe(III) molar ratio of 1:2 are shown in Figure 30, while Figure 31 shows the results for the same system with 15.8 ppm of NaLS substituted for the collector.

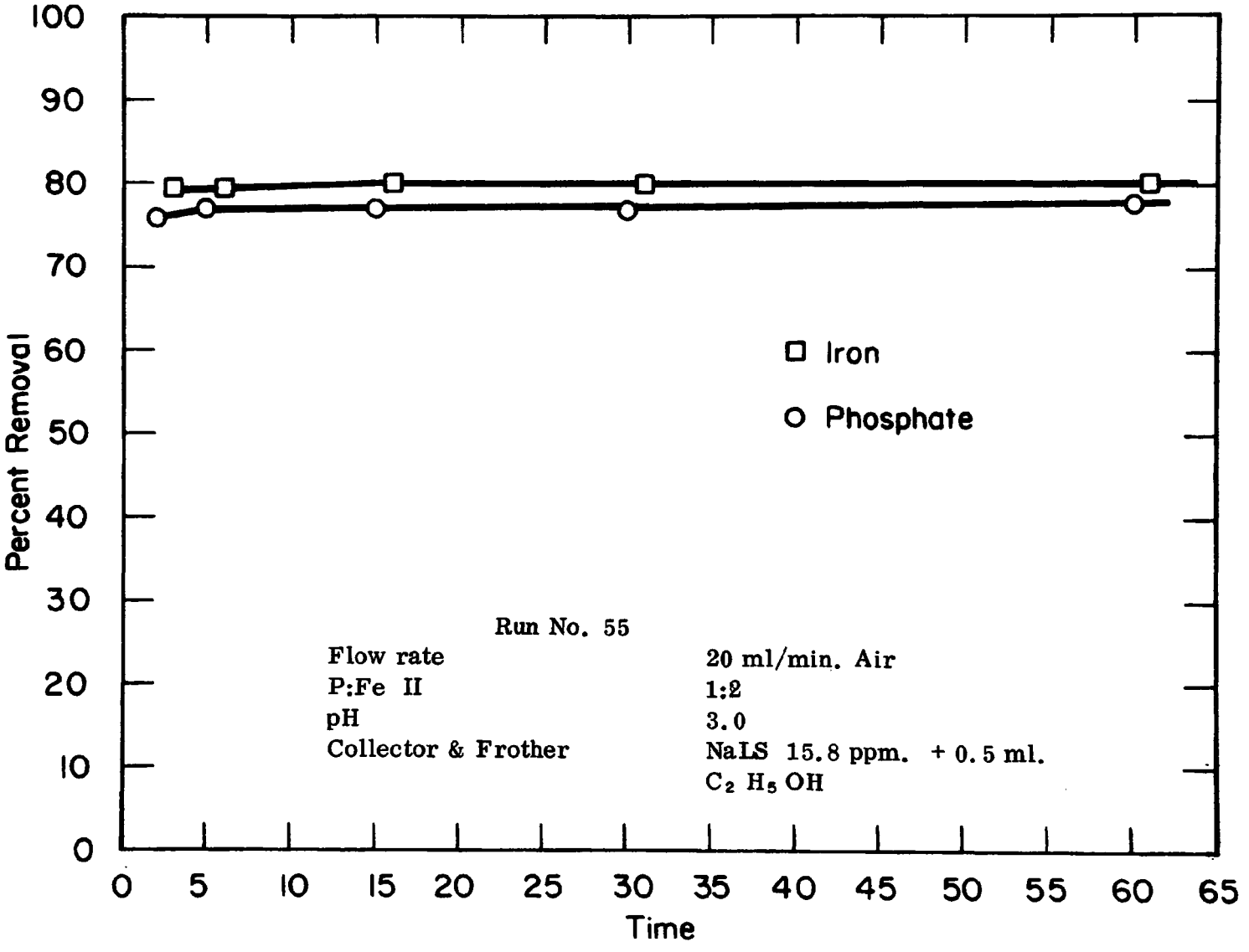


Figure 29. Time vs per cent removal.

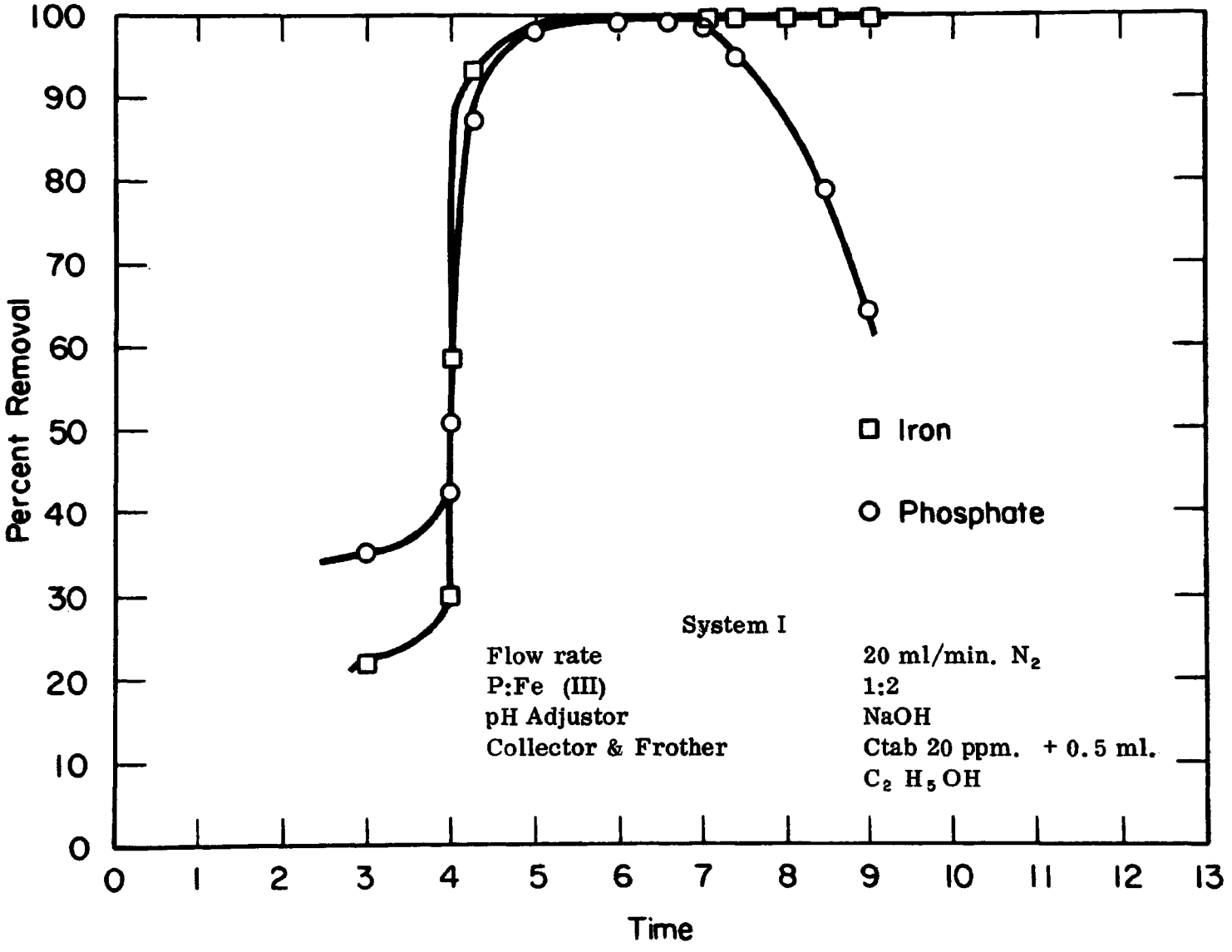


Figure 30. pH vs per cent removal.

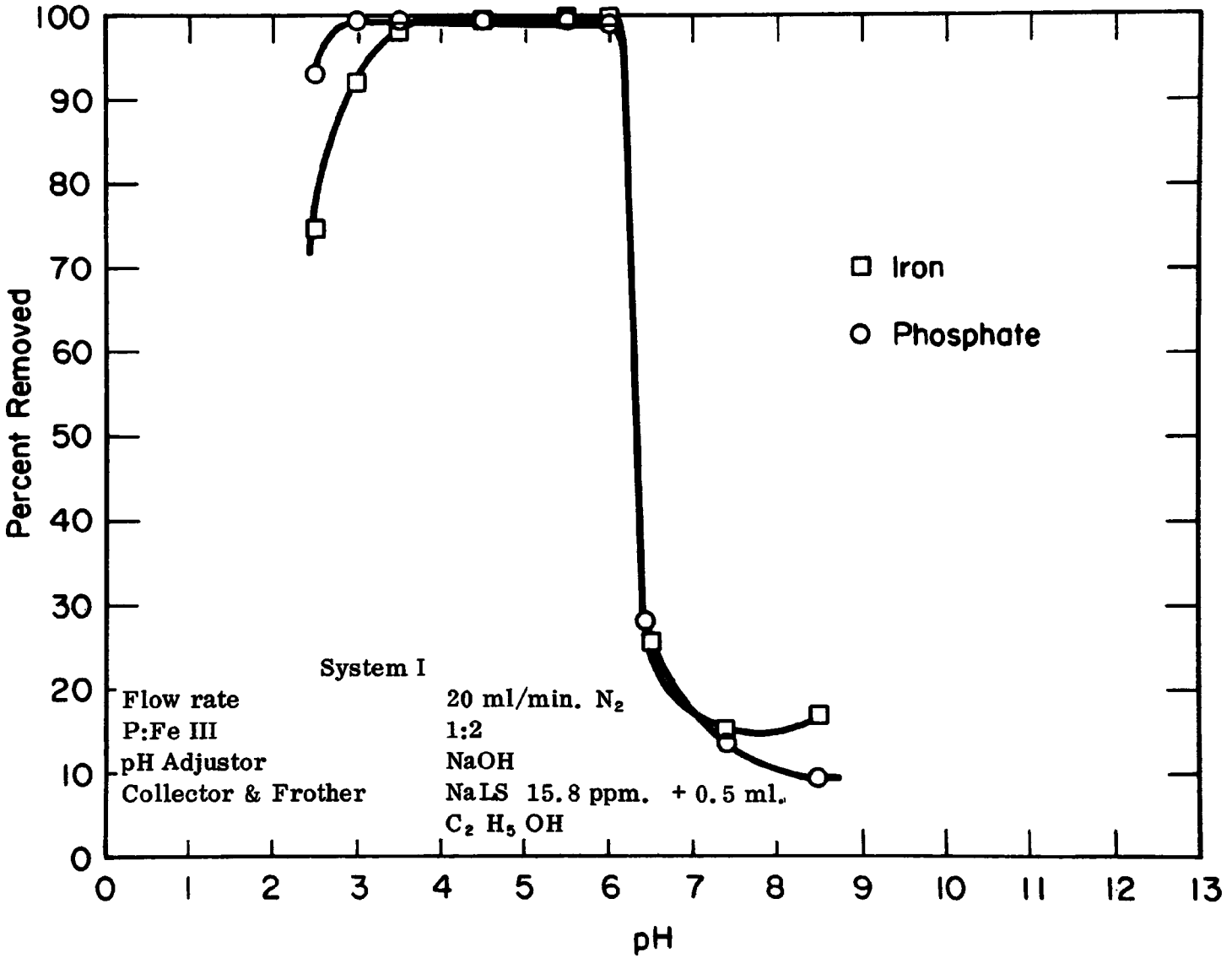


Figure 31. pH vs per cent removal.

In Figure 32, iron and phosphate removals are plotted against PO_4:Fe molar ratio for a pH value of 7.4, with 20 ppm Ctab as the collector, and a similar plot is shown in Figure 33, for a pH value of 4.5 and 15.8 ppm NaLS as the collector.

The removal by microflotation of phosphorous and iron as a function of pH (Figures 30 and 31) may be compared with removals by sedimentation in the same system, shown in Figure 34.

(b) System II

In this system, ferrous sulfate was used as the coagulant, nitrogen as the gas phase, and sodium hydroxide for pH adjustment. Both Ctab and NaLS were employed as collectors. Quantitatively, the system components were:

KH_2PO_4	35 ppm as PO_4
$FeSO_4$	41.17 ppm as Fe(II)
NaOH	as required
N_2	20 ml/min.

Figure 35 shows the results when using 20 ppm Ctab as the collector and 0.5 ml C_2H_5OH as the frother, while Figure 36 presents the results when 15.8 ppm NaLS was used as the collector, with 0.5 ml C_2H_5OH as the frother. A removal versus pH curve for the same system under sedimentation conditions is shown in Figure 37.

(c) System III

In this system, ferrous sulfate was used as the coagulant, air as the gas phase, and sodium hydroxide for pH adjustment. Both Ctab and NaLS were employed as collectors. Quantitatively, the system components were:

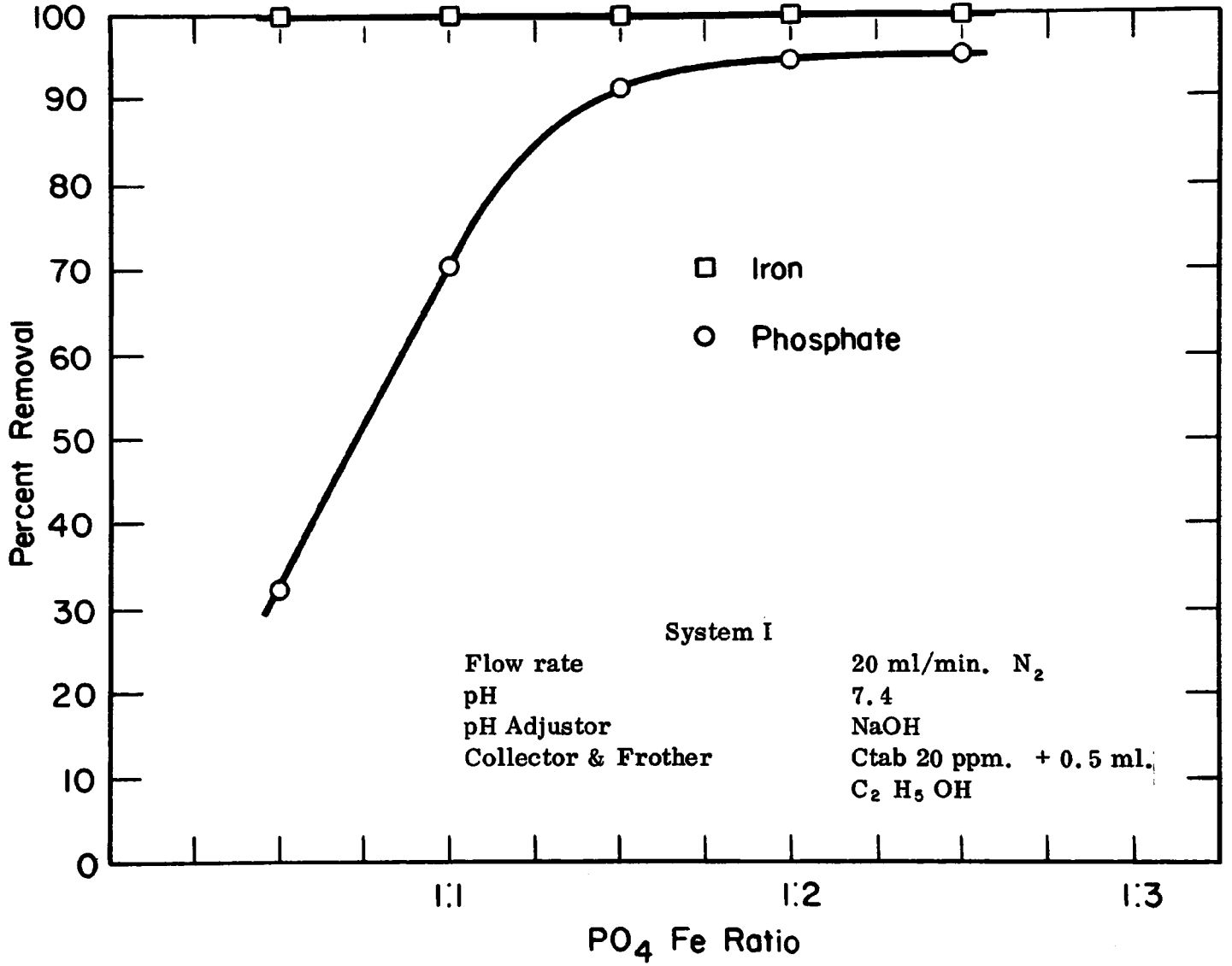


Figure 32. PO_4 :Fe ratio vs per cent removal.

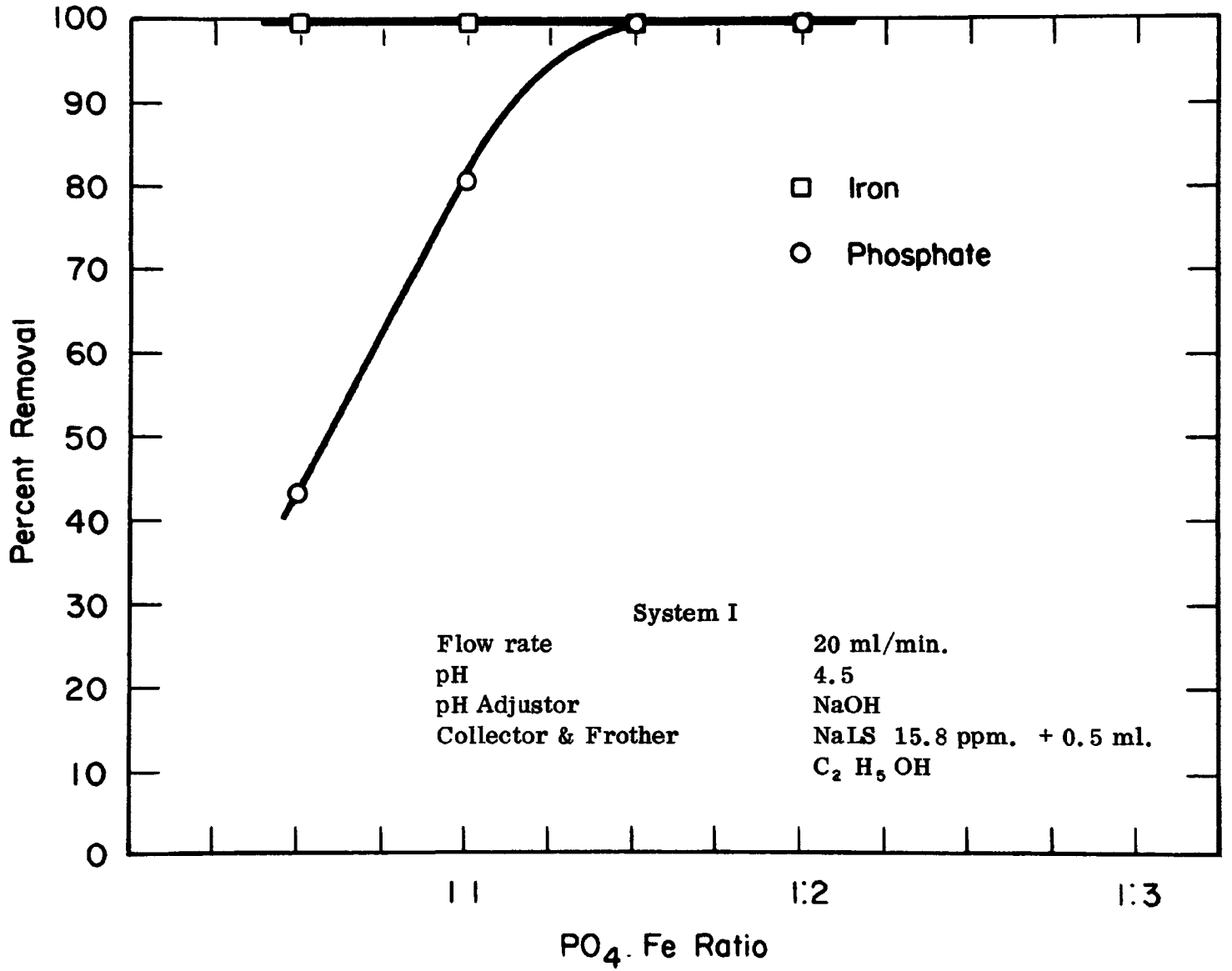


Figure 33. PO_4 :Fe ratio vs per cent removal.

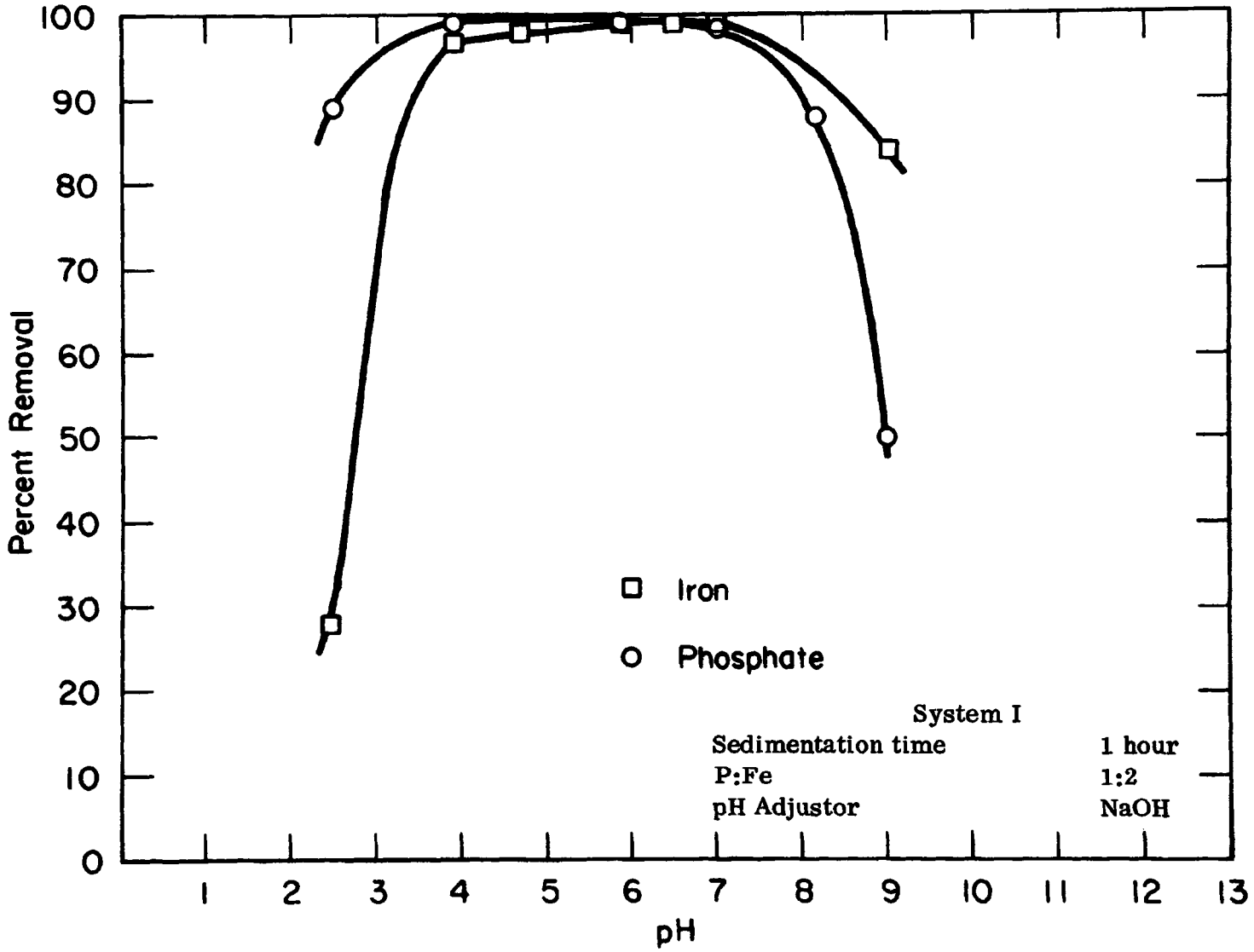


Figure 34. pH vs per cent removal.

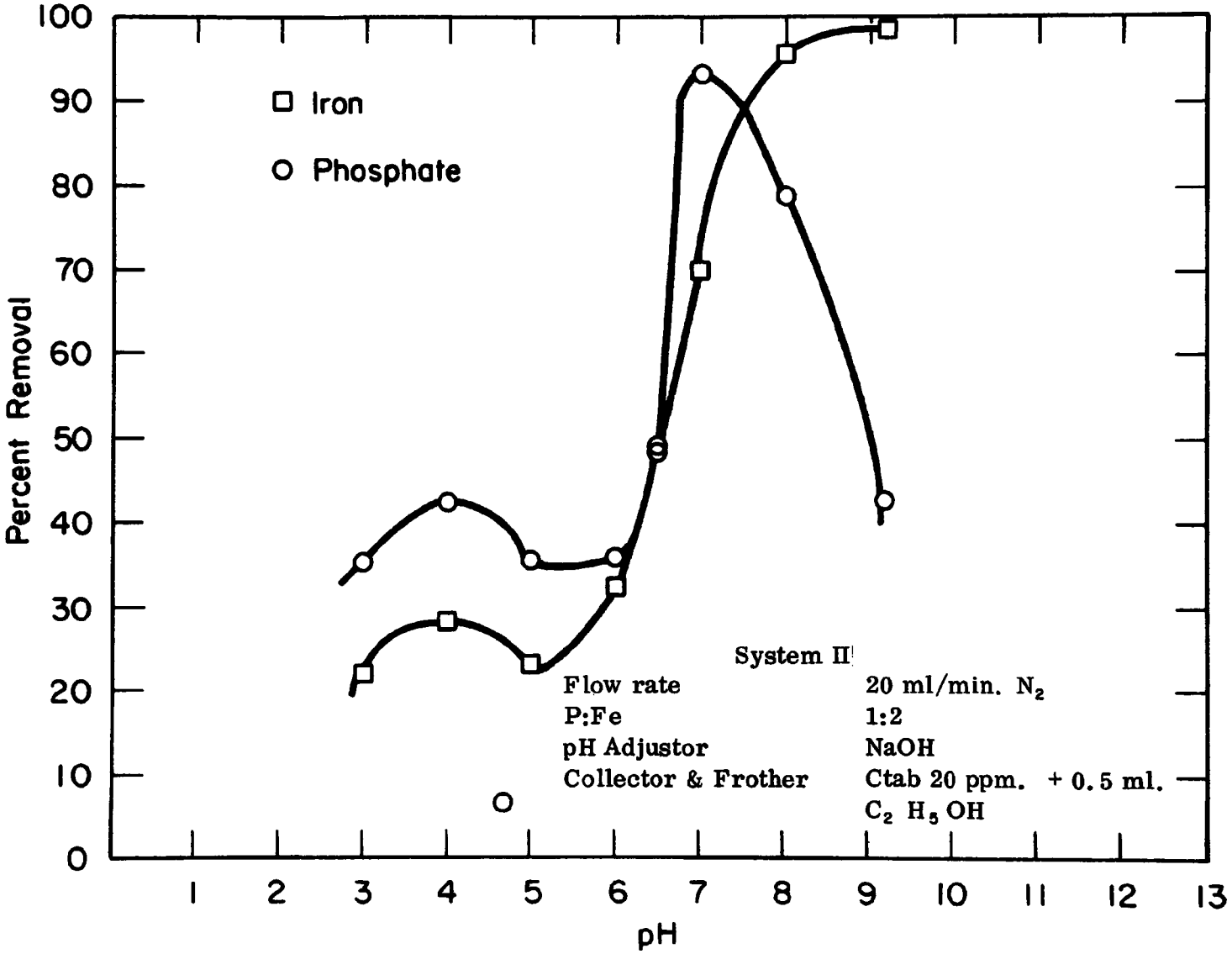


Figure 35. pH vs per cent removal.

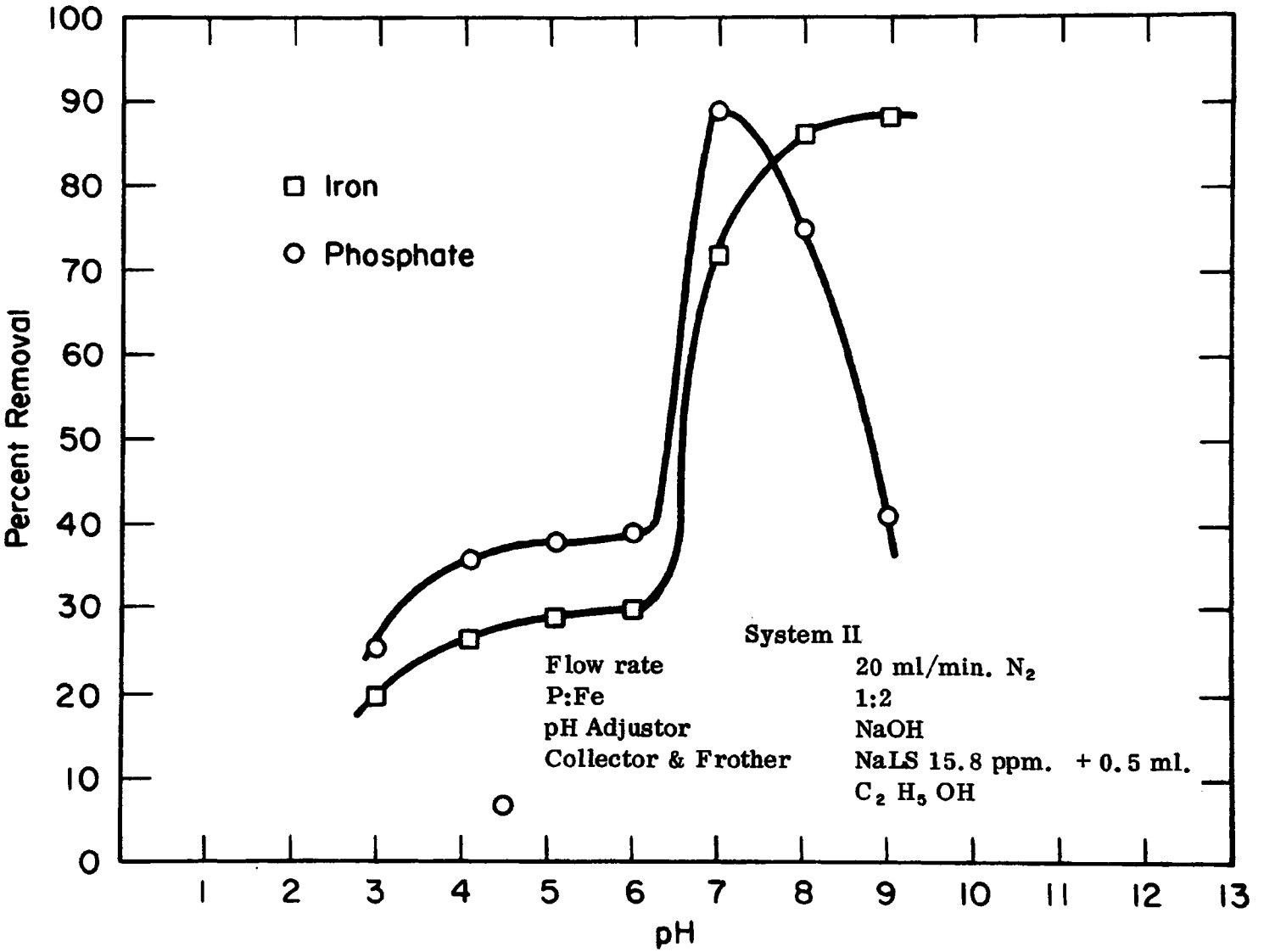


Figure 36. pH vs per cent removal.

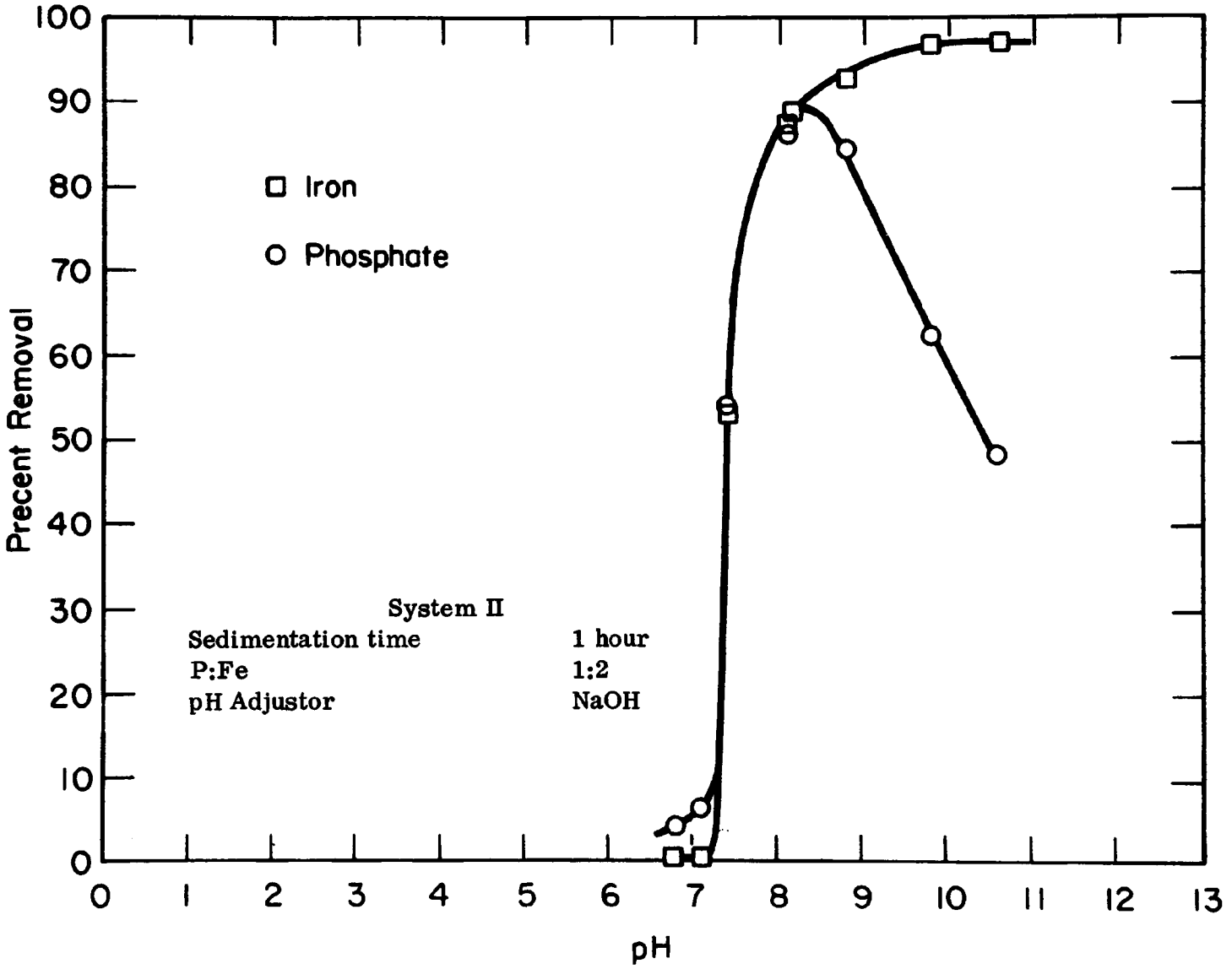


Figure 37. pH vs per cent removal.

KH_2PO_4	35 ppm as PO_4
$FeSO_4$	41.17 ppm as Fe(II)
NaOH	as required
Air	20 ml/min

Figure 38 shows the results when using 20 ppm Ctab as the collector and 0.5 ml C_2H_5OH as the frother, while Figure 39 shows the results for the same system when using 15.8 ppm NaLS as the collector in place of the Ctab.

(d) System IV

System IV differed from System III in that calcium hydroxide, rather than sodium hydroxide, was used as the reagent for pH adjustment. As in System III, ferrous sulfate was used as the coagulant, air was employed as the gas phase, and both Ctab and NaLS were used as collectors. Quantitatively, the system components were:

KH_2PO_4	35 ppm as PO_4
$FeSO_4$	as required to give the desired P:Fe molar ratio
$Ca(OH)_2$	as required
Air	20 ml/min

Figure 40 shows the results obtained using 20 ppm Ctab, 0.5 ml C_2H_5OH, and a P:Fe(II) molar ratio of 1:2, and Figure 41 shows the results obtained using 15.8 ppm NaLS, 0.5 ml C_2H_5OH, and a P:Fe(II) molar ratio of 1:2. Figures 42 and 43 show removals versus PO_4:Fe molar ratio for the Ctab and NaLS collector systems, respectively. The pH maintained for the data of Figure 42 was 7.0, while the pH value for the data of Figure 43 was 10.

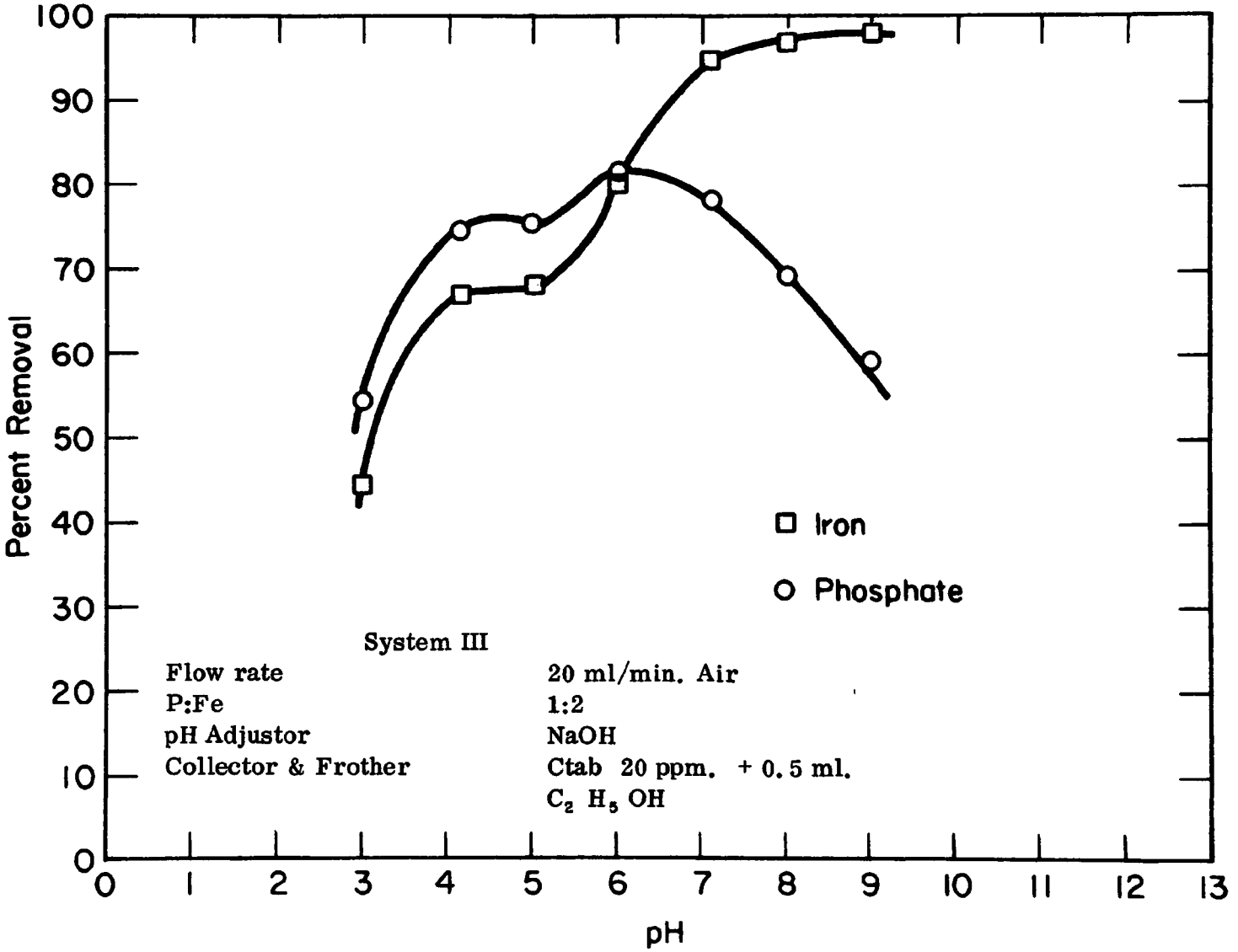


Figure 38. pH vs per cent removal.

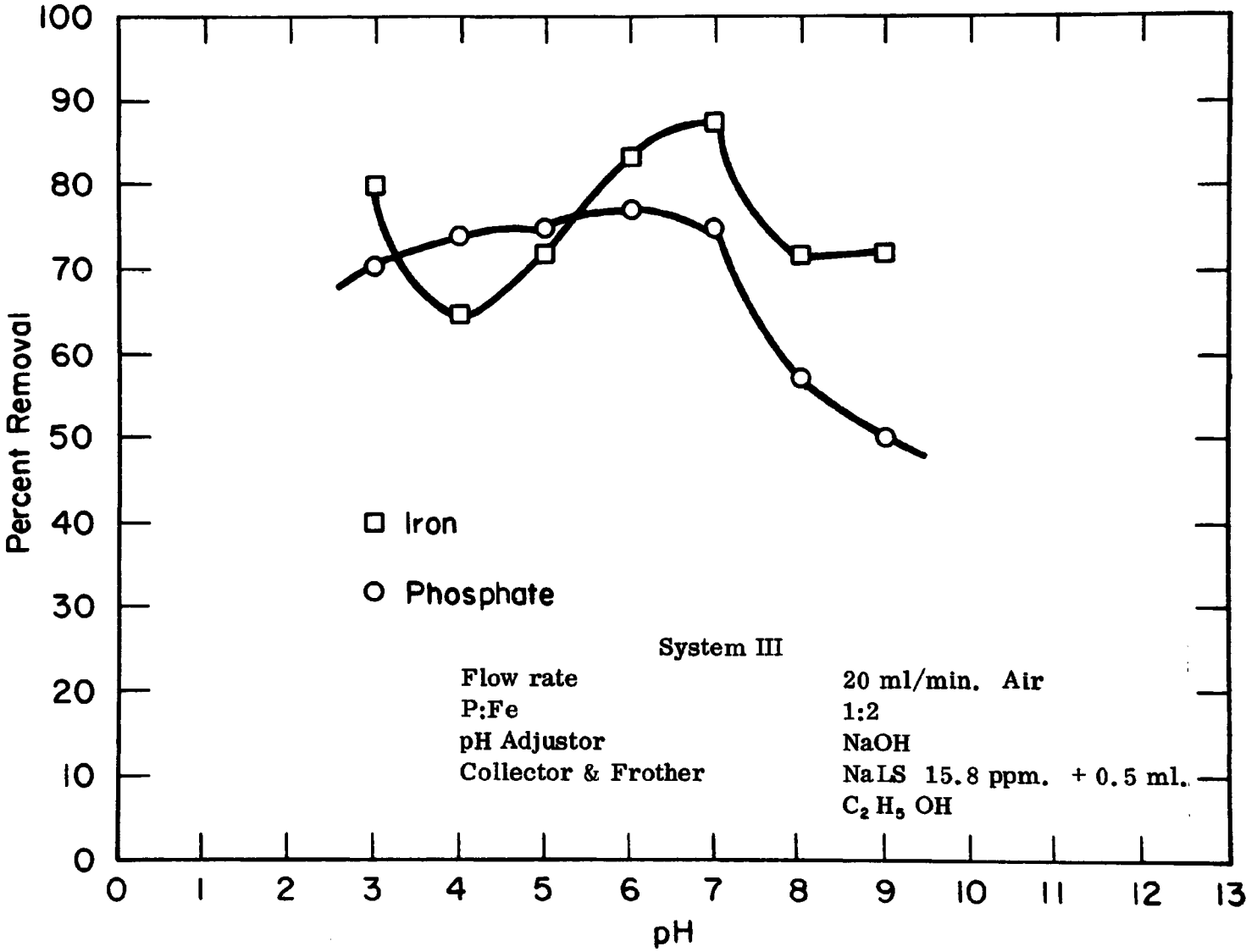


Figure 39. pH vs per cent removal.

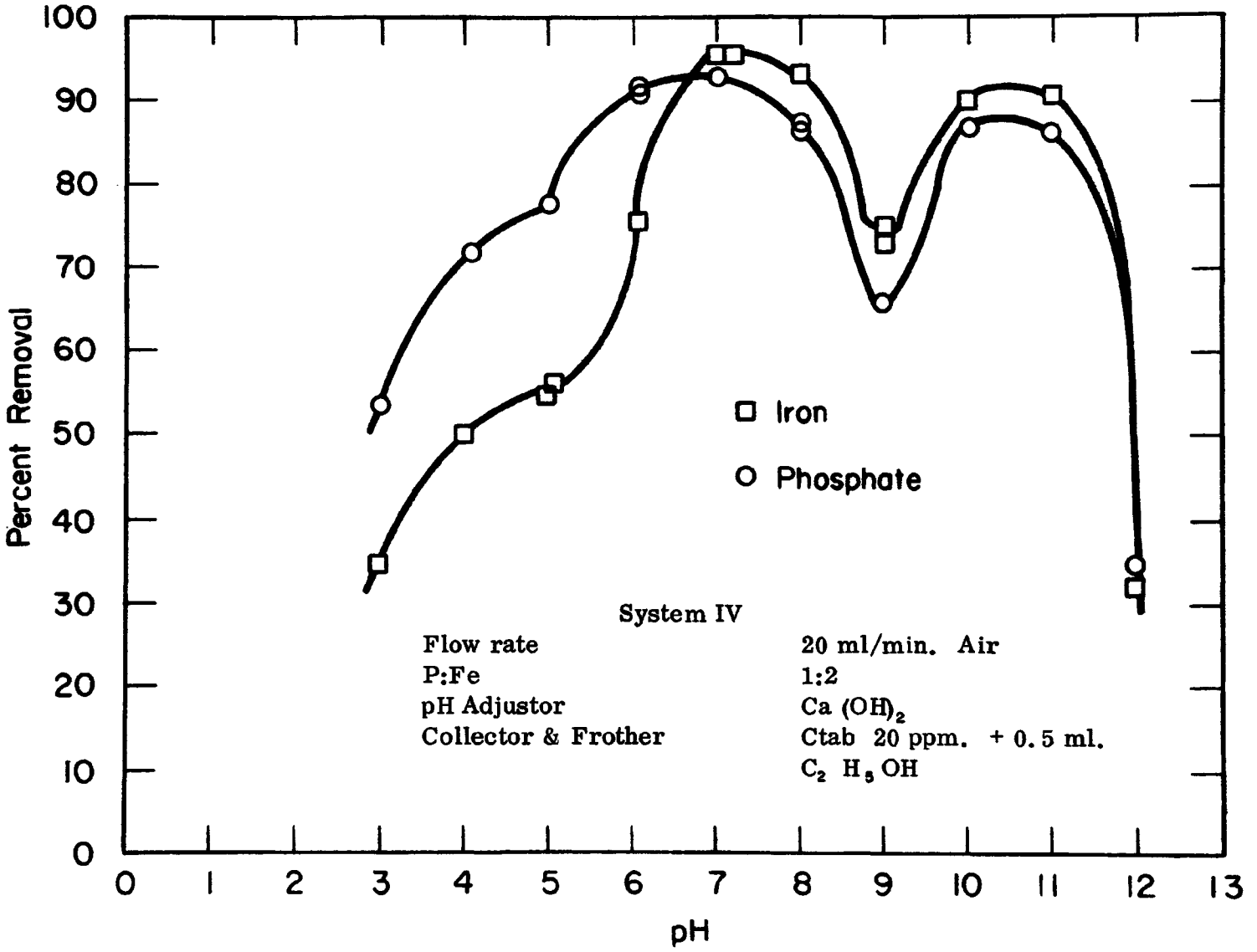


Figure 40. pH vs per cent removal.

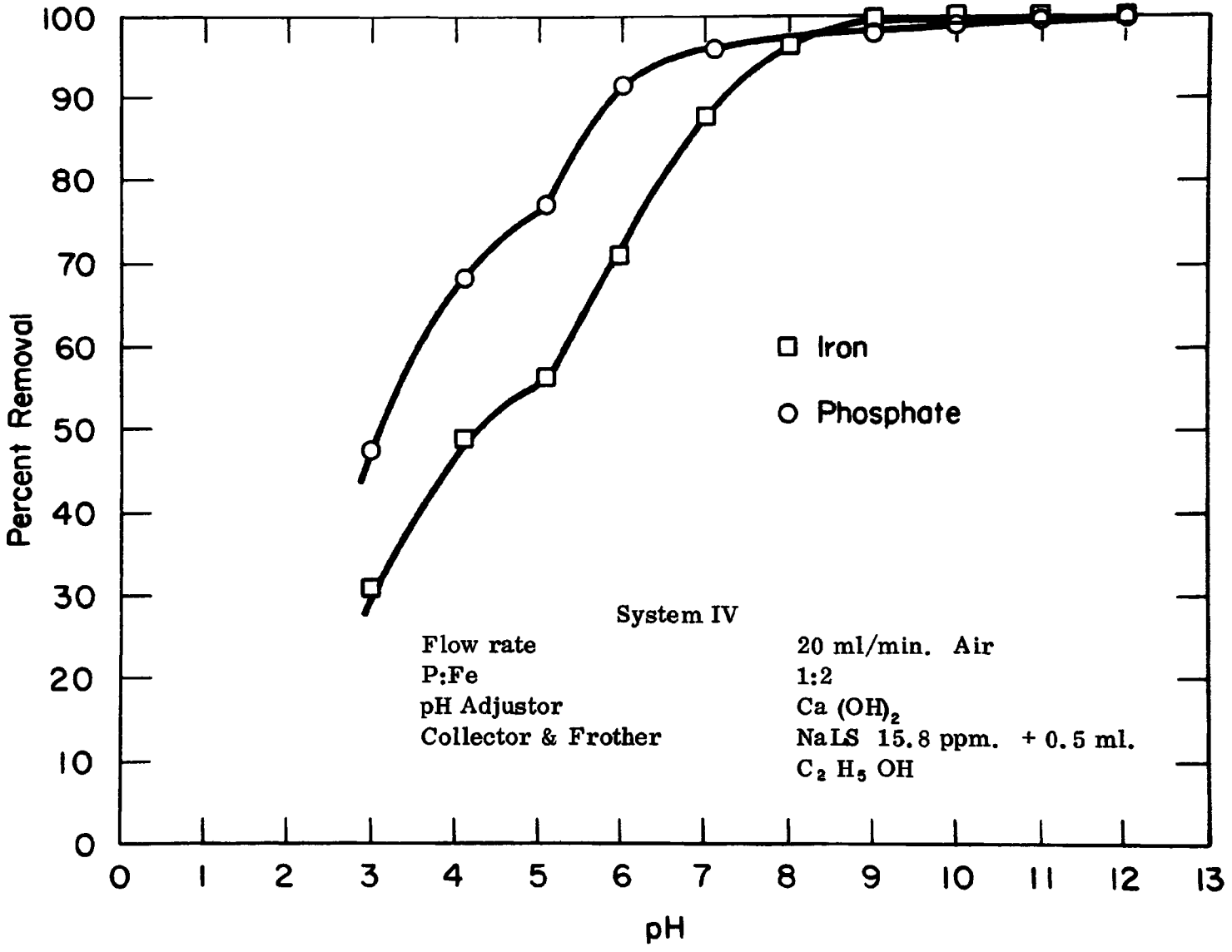


Figure 41. pH vs per cent removal.

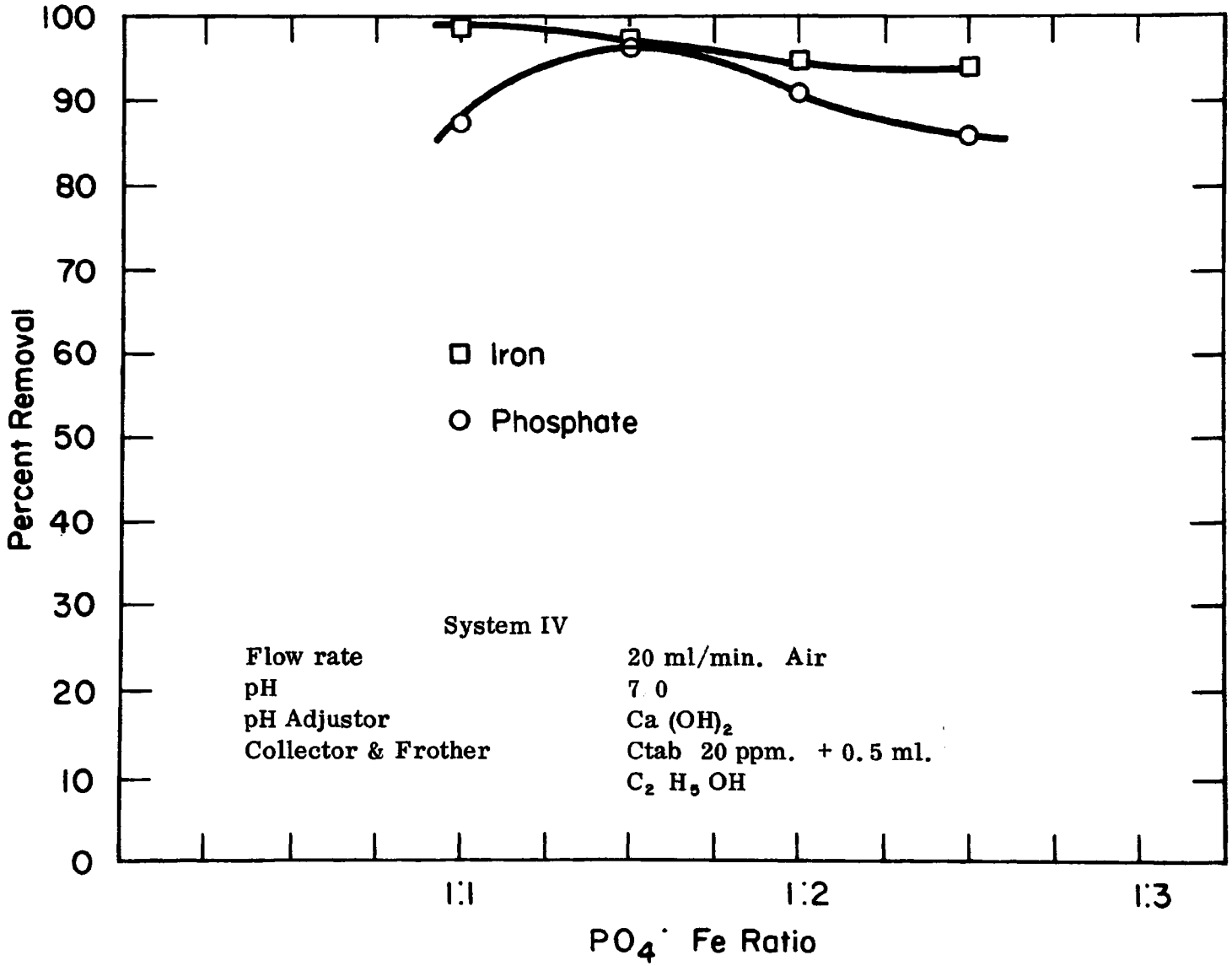


Figure 42. PO_4 :Fe ratio vs per cent removal.

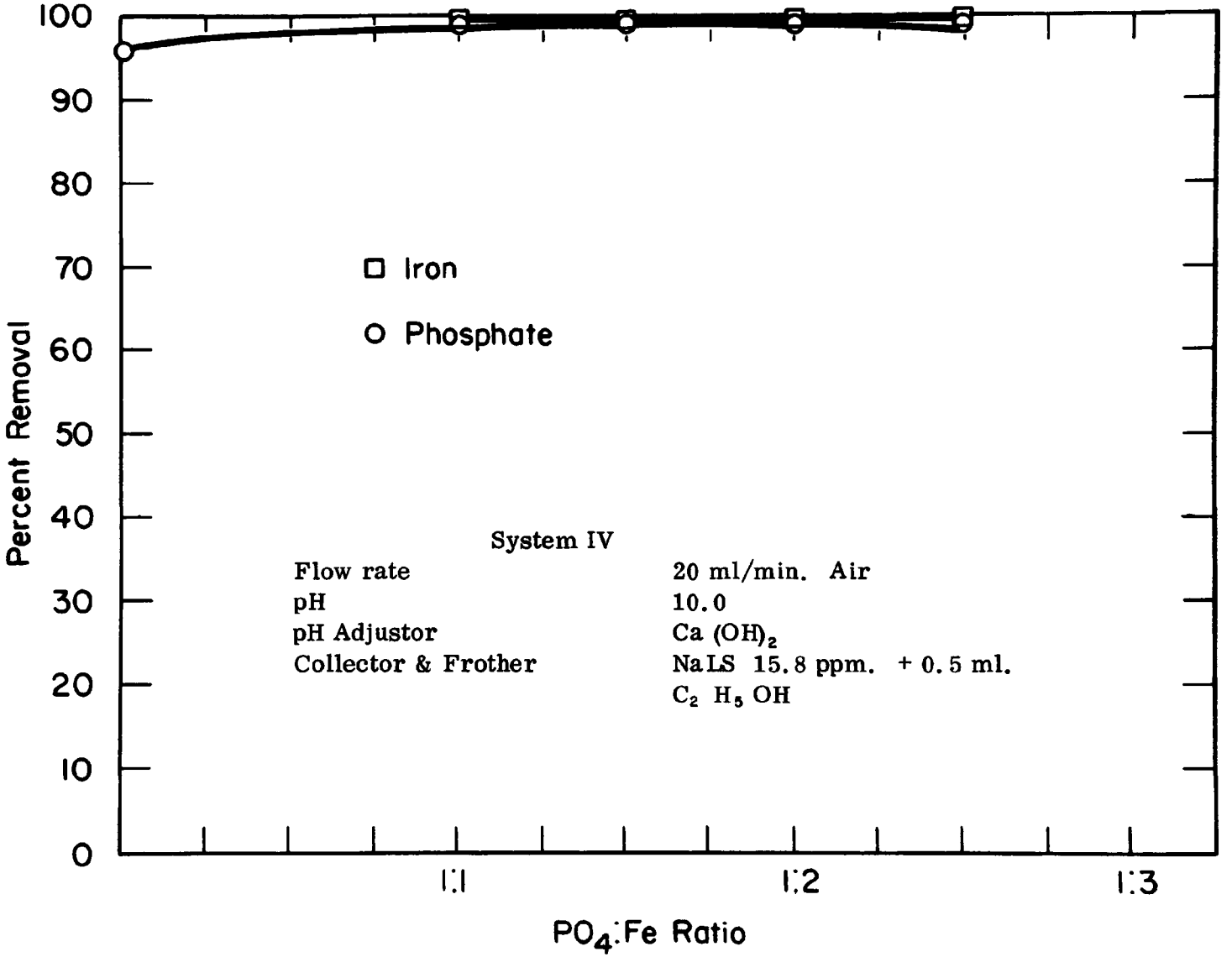


Figure 43. PO_4 :Fe ratio vs per cent removal.

Figures 44 and 45 show the effect of varying the collector concentration. In Figure 44, the collector used was Ctab, the P:Fe(II) molar ratio was 1:2, and the pH was adjusted to a value of 7.0 with $Ca(OH)_2$ while in Figure 45, NaLS was used, the P:Fe(II) molar ratio was 1:2, and $Ca(OH)_2$ was used to adjust the pH to 10.0.

(e) System V

In system V, no coagulant was used. Instead, the removal of phosphate by lime alone was studied over a range of pH values, with both Ctab and NaLS being used as collectors. Quantitatively, the system components consisted of:

KH_4PO_4	35 ppm as PO_4
$Ca(OH)_2$	as required
Air	20 ml/min

Figure 46 shows phosphate removal versus pH when using 20 ppm Ctab, with 0.5 ml C_2H_5OH, while Figure 47 shows the results when using 15.8 ppm NaLS, with 0.5 ml C_2H_5OH.

The results of precipitation experiments made on the ortho-phosphate-calcium hydroxide system (presented in Section 4. indicate that the amount of calcium hydroxide added for pH adjustment up to a pH of 9 is the amount required only to neutralize the system. This suggests that calcium hydroxide does not form a phosphate precipitate until a pH of 9 or above is reached.

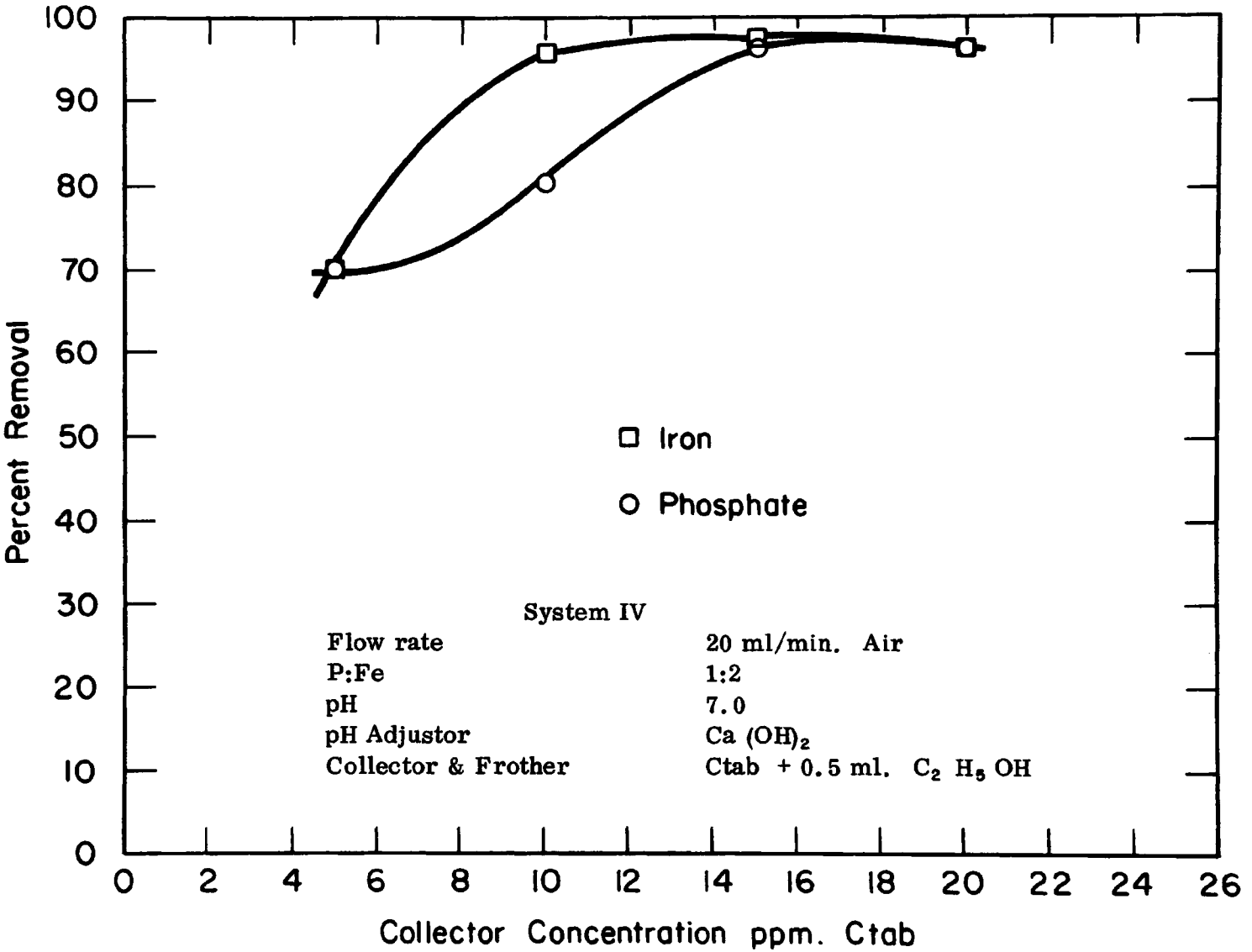


Figure 44. Per cent removal vs collector concentration.

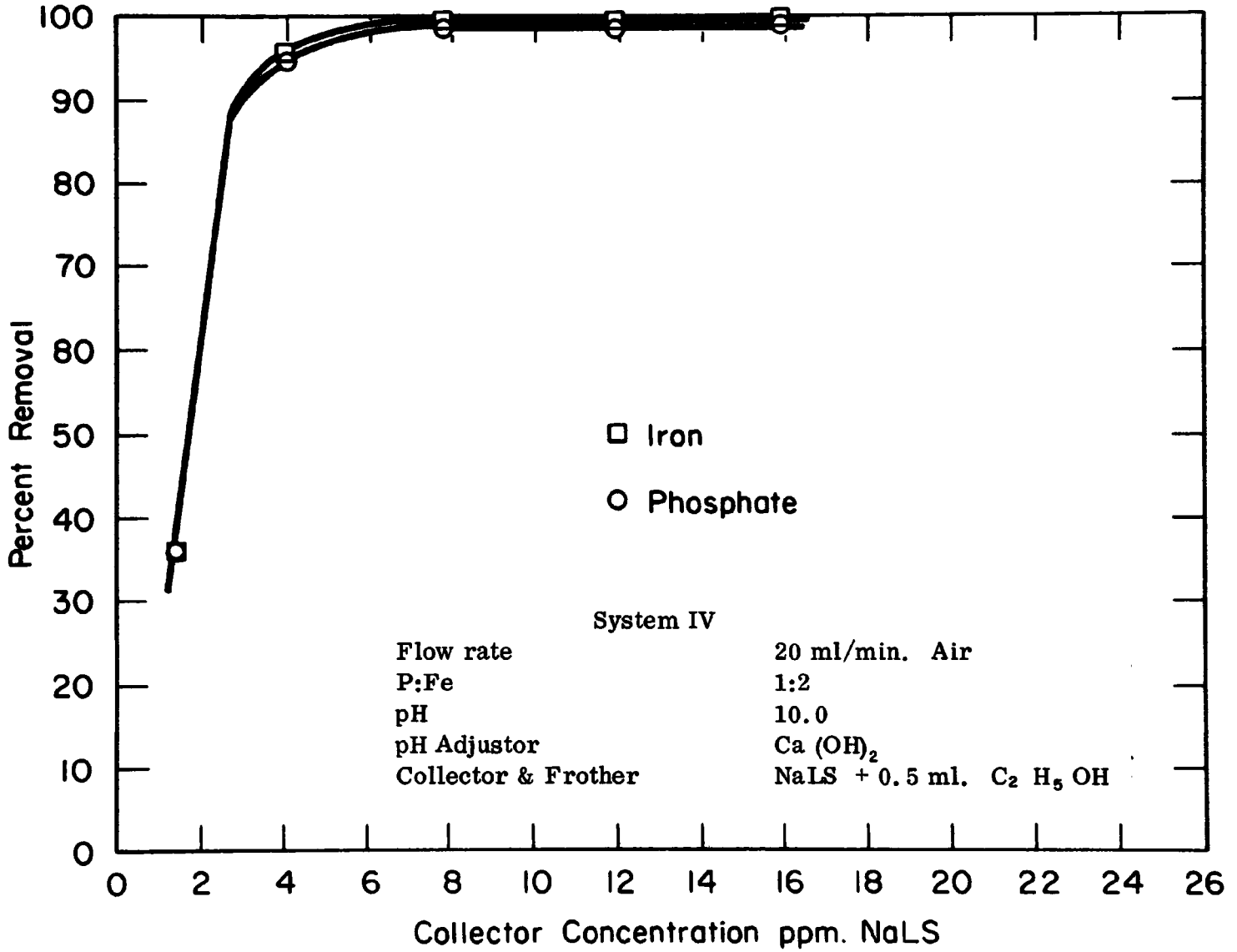


Figure 45. Per cent removal vs collector concentration.

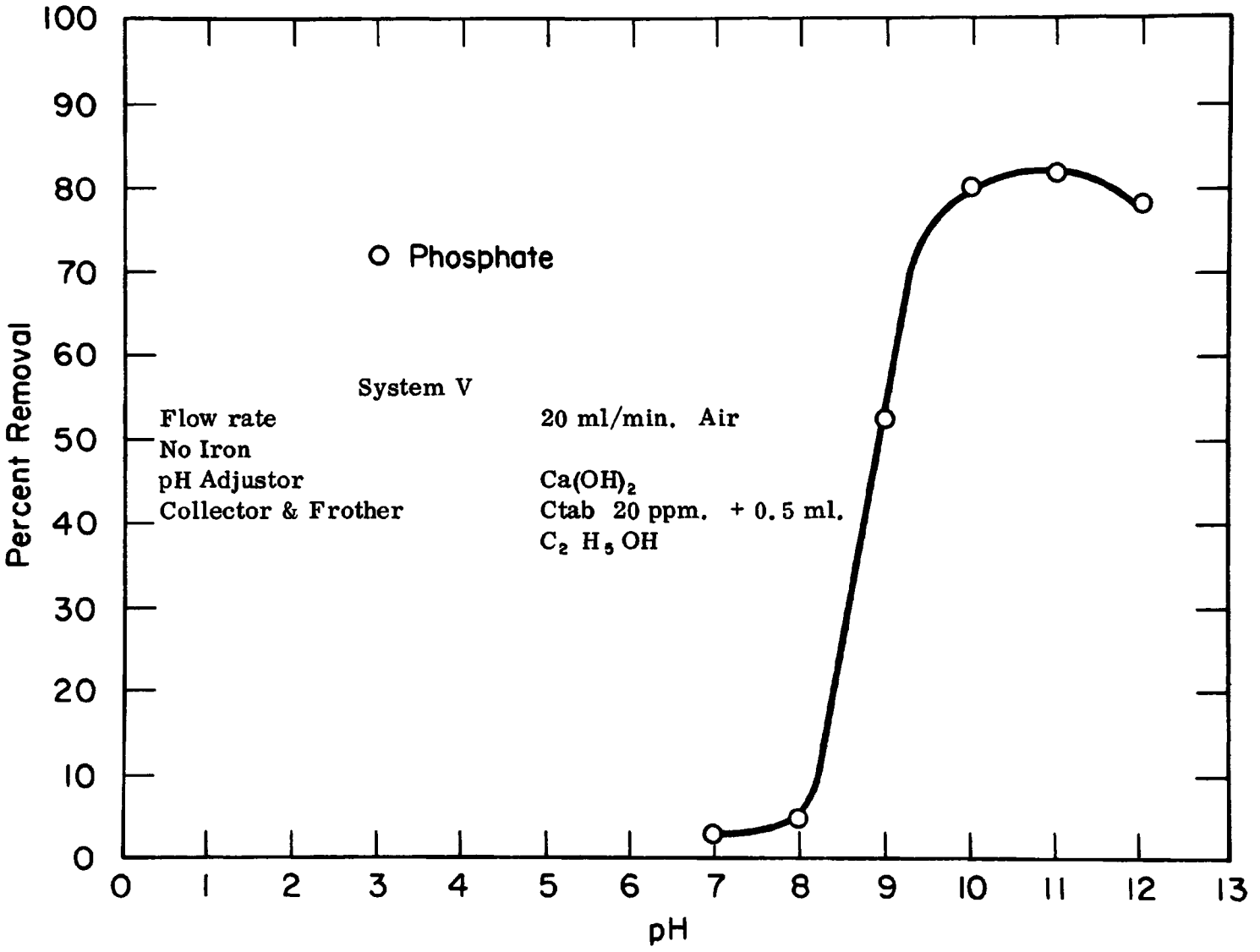


Figure 46. pH vs per cent removal.

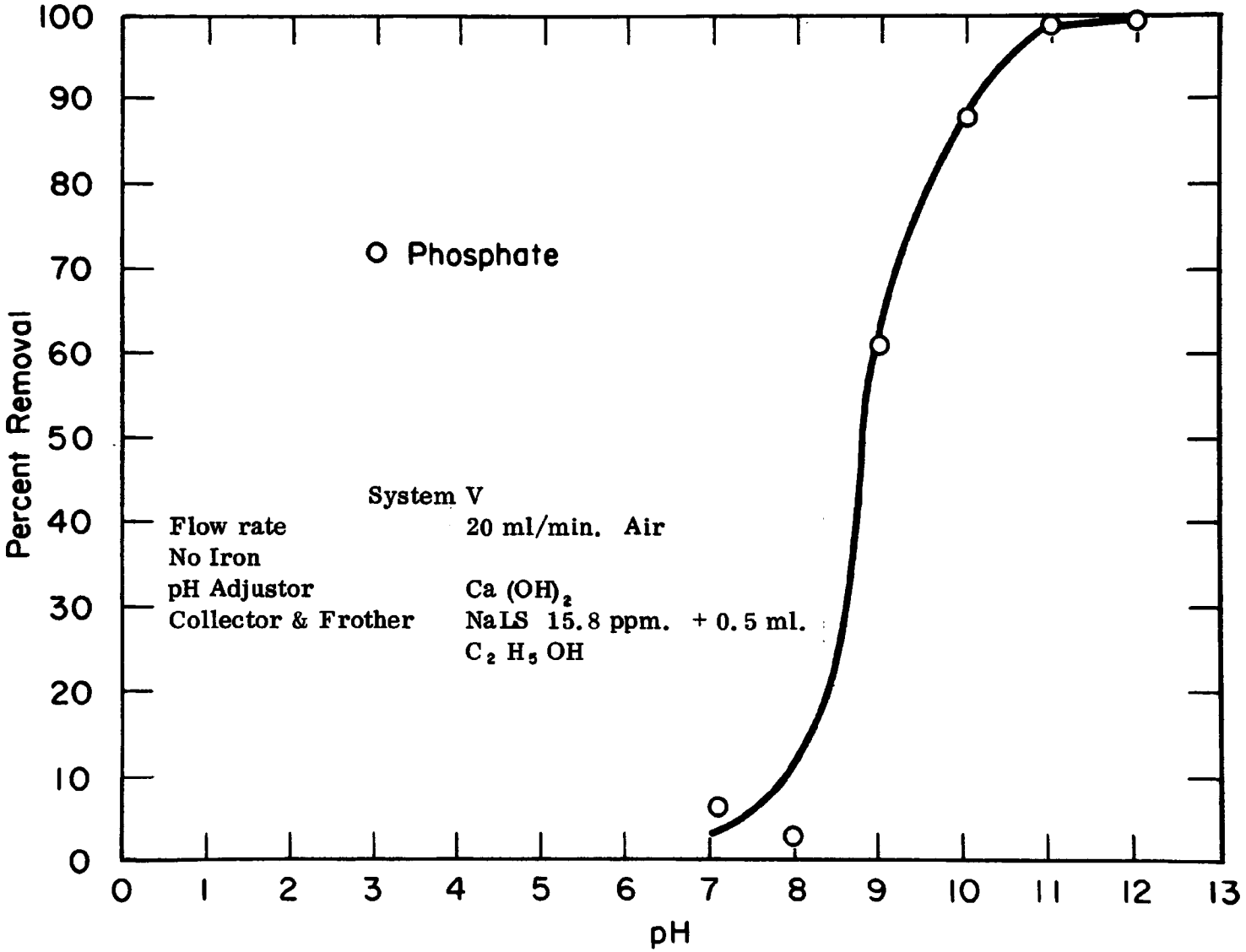


Figure 47. pH vs per cent removal.

Conclusions

A. System I

1. 99 percent phosphate removal can be achieved by flotation with 20 ppm Ctab in the pH range from 5.2 to 7.0.
2. Over 99 percent phosphate removal is possible by flotation with 15.8 ppm NaLS in the pH range from 3.0 to 6.0.
3. The optimum phosphate to iron molar ratio occurs at a ratio of 1:1.5, for flotation by both Ctab and NaLS.

B. System II

1. A close correspondence between the flotation curves by Ctab and NaLS and the sedimentation curve indicates the removal of a ferrous phosphate compound at pH 7.0.
2. At pH 7.0, 93 percent and 89 percent phosphate removal is achieved by flotation with Ctab and NaLS respectively.

C. System III

1. Maximum removals of phosphate of 81 percent and 74 percent are achieved by flotation with Ctab and NaLS respectively at pH 7.0
2. The removal characteristics of System III appear to be comprised of a combination of the properties of System I (ferric iron) and System II (ferrous iron), The collector adsorption characteristics display the properties of System II at low pH values and the properties ofSystem I in the high pH range.

D. System IV

1. Two maximums appear in the phosphate removal curve by flotation with Ctab. The first peak with 93 percent removal at pH 7.0 is attributed to the removal of a ferric-phosphate compound. The second peak with 87 percent removal at pH 10.5 is attributed to the removal of a calcium phosphate compound.
2. Flotation of phosphate with NaLS produces 99 percent removal above pH 10.0. The collector efficiency of NaLS is distinctively superior to Ctab in this system.
3. The optimum phosphate to iron molar ratio was found to be around 1:1.5 for flotation with Ctab at pH 7.0. The removal of phosphate using NaLS was independent of the iron concentration above pH 10.0 using calcium hydroxide as the pH adjustor.
4. The optimum collector concentration for Ctab is around 10 ppm at pH 7.0. This corresponds to a 1:0.075 molar ratio of phosphate to collector.
5. The optimum collector concentration for NaLS for pH 10.0 is 5 ppm corresponding to a phosphate to collector molar ratio of 1:0.047.

E. System V

1. Removal of phosphate by calcium hydroxide addition and flotation with Ctab produced a maximum removal of 83 percent at pH 11.0.
2. Phosphate removal, floating with NaLS, reached 99 percent removal at pH 11.0.

F. General

1. The best removals using iron sulfate and sodium hydroxide may be achieved with a ferric sulfate molar concentration of 1.5 times that of phosphate in a pH range from 2.5 to 7.5. NaLS proved to be the better collector below pH 5.0 and Ctab displayed better removal characteristics above pH 6.0.
2. Although 90 percent phosphate removal is achieved in a narrow pH range around pH 7.0 by the addition of ferrous sulfate, oxidation of the iron with air to produce ferric sulfate lowers the percent removals but increases the pH range. The removals varied between 70 to 80 percent using both NaLS and Ctab in the pH range from pH 3 to pH 7.
3. The best removals for calcium hydroxide addition were achieved by using NaLS above pH 10.0. The limiting factors in the removal of phosphate by calcium hydroxide are the large concentrations of the calcium hydroxide required and the resulting high pH values of the solution.

Dissolved Air Flotation

Dissolved air flotation of insoluble floc differs from microflotation in that the small gas bubbles which carry the floc to the surface are produced by releasing dissolved gas from solution, rather than by using a diffusor. A commonly used procedure is to dissolve the gas under pressure, and then reduce the pressure on the fluid back to atmospheric

when the floc suspension enters the flotation tank, allowing the dissolved gas to come out of solution in the form of small bubbles. Through this procedure, the need for a frothing agent is often eliminated. However, a surface active collector is often used as in the case of microflotation.

The experiments described below were conducted to investigate the efficiency of dissolved air flotation of floc generated in the coagulation and precipitation of phosphate from solution by Fe(II). Three collectors were studied; Ctab (Hexadecyl tri-methyl ammonium bromide), NaL (sodium laurate), and Duomac C (N-coco-1,3 diaminopropane acetate). Duomac C, a diamine, and Ctab, a quaternary ammonium salt, are cationic surfactants while NaL, a sodium salt of lauric acid, is an anionic surfactant. The major variables studied were the affective pH range of the collector, recycle ratio, and the P:Fe molar ratio. pH adjustment was accomplished by the addition of $Ca(OH)_2$, and Fe(II) was added in all experiments as ferrous sulfate.

Apparatus and Procedure

The flotation system used in this study is shown in Figure 48. The equipment consists of a 1200 cc pressurization chamber fitted with a quick connect coupling for admission of the 40 psi air supply. The pressurization chamber is constructed of an acrylic resin tube, 14 inches long with a 3-inch inside diameter and half-inch walls. The ends are made of 6 inch by 6 inch by 1/2-inch 316 stainless steel. A

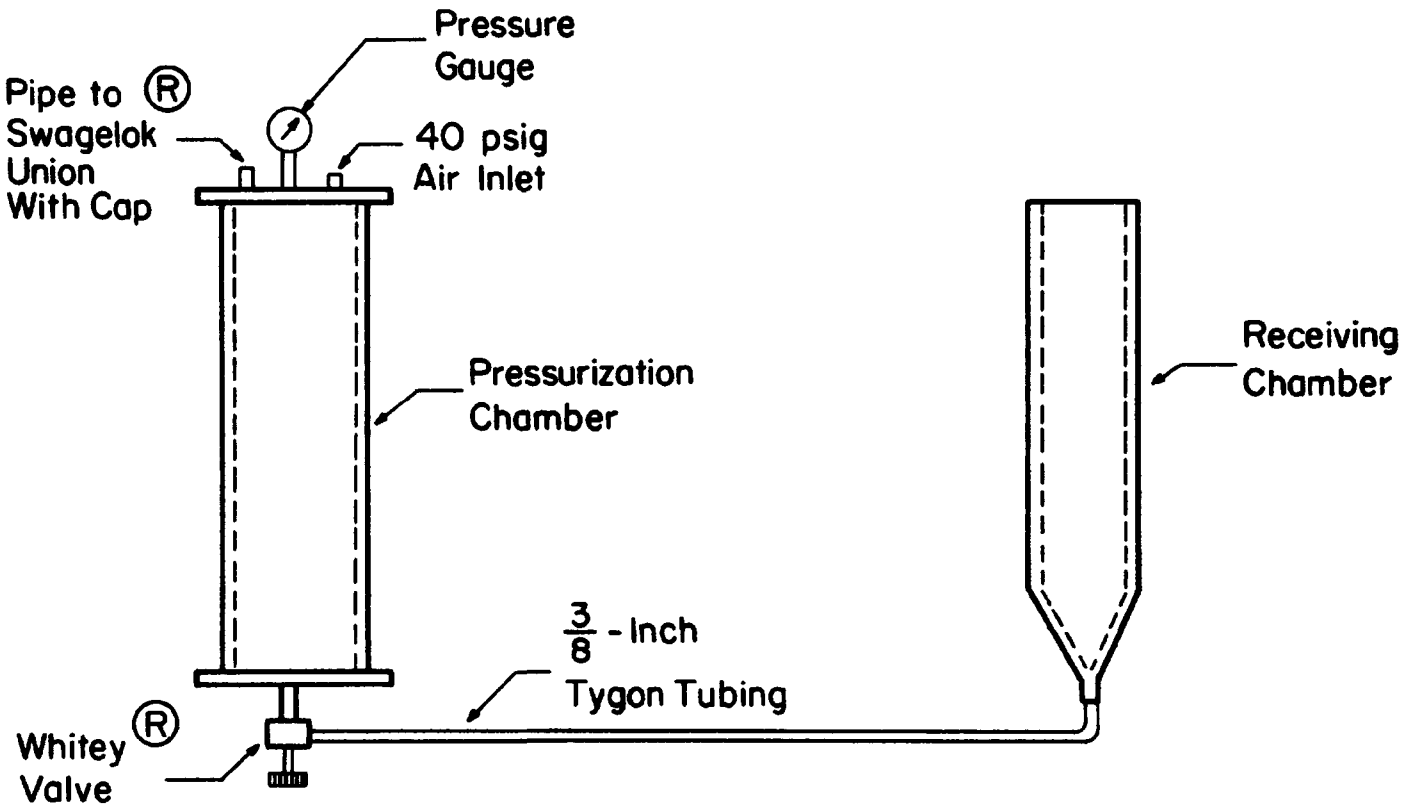


Figure 48. Dissolved air flotation system.

neoprene rubber gasket was placed in the machined seat for a tight seal between the tube and the stainless steel plate. The top plate was fitted with the quick connect coupling, a pipe to "Swagelok" union with a "Swagelok" cap for pressure release, and a 0- 60 psi pressure gauge. The bottom plate contained a 3/8 inch "Whitey" 90° valve.

The receiving chamber also has a volume of approximately 1200 cc. It is constructed of pyrex glass with a 3-inch inside diameter. At the bottom the chamber is conical in shape with a 3/8-inch outside diameter inlet. This shape gave the best mixing conditions when the air-liquid mixture entered the chamber which contained the test solution.

The amounts and types of reagents used in this study varied, but the sequency of addition remained the same. Initially, 450 ml of distilled water was placed in a clean 1000 ml pyrex beaker. The phosphate make-up solution was then added, followed by addition of solid $FeSO_4 \cdot 7H_2O$ as required for the test. The solution was stirred and allowed to stand for 3 or 4 minutes to insure dissolution of the iron salt. The pH was then adjusted with a 0.2 N suspension of calcium hydroxide. pH stabilization usually required ten to fifteen minutes. Following adjustment of the pH, the prescribed amount of surfactant was added to the system, along with sufficient distilled water to provide a total solution of 500 ml.

A dissolved air solution was prepared by first adding 1000 ml of distilled water into the pressurization chamber via the pipe to "Swagelok" union. After the water was added the union was capped and the 40 psi air supply connected. To assure complete saturation, the air-water

mixture was shaken 5 or 6 times at intervals of about 1 minute. When saturation was reached, tygon tubing was connected to the outlet of the Whitey valve and to the inlet of the receiving chamber.

Before adding the test sample in the receiving chamber, the mixture was gently stirred to create a uniform distribution of the floc. Immediately after placing the sample in the receiver, the valve was opened 1/4 turn to allow the air-water solution to enter the receiver. The shearing action through the valve and the reduction to atmospheric pressure, permitted formation of minute air bubbles before the air-liquid mixture enters the receiving chamber. The amount of the air-water mixture added depends on the recycle ratio desired, where the recycle ratio is defined as the amount of influent (air-water mixture) expressed as a percentage of the sample solution (500 ml).

Following flotation of the floc, the tygon tubing was disconnected from the "Whitey" valve and about 80 percent of the effluent was drained into a clean beaker. Samples for analysis were taken from this beaker via pipet.

Reagents

Data for the four systems studied will be presented separately. The data plots shown are intended only to identify the conditions required for effective phosphate and iron removal, with pH, coagulant concentration, choice of collector, and recycle ratio being the major process variables. For a discussion of the results in terms of the fundamental chemical considerations involved, the reader is referred to Dietz (21).

(a) System Ia

In this system, the effectiveness of both Duomac C and NaL as collectors were studied over a range of pH values. Quantitatively, the system components were:

KH_2PO_4	35 ppm as PO_4
$FeSO_4$	41.22 ppm as Fe(II)
$Ca(OH)_2$	as required for pH adjustment
Collector	20 ppm
Recycle Ratio	100 percent

Figure 49 shows the removal of iron and phosphate versus pH when Duomac C is used as a collector, while Figure 50 shows the results when NaL is used as a collector.

(b) System IIa

In this system, all three collectors were studied over a range of concentrations. Quantitatively, the system components were:

KH_2PO_4	35 ppm as PO_4
$FeSO_4$	41.22 ppm as Fe(II)
$Ca(OH)_2$	as required for pH adjustment
Recycle Ratio	100 percent
Collector	Variable

Figure 51 shows a plot of iron and phosphate removal at pH 7 versus Ctab concentration, Figure 52 shows removal versus NaL concentration at pH 7, and Figure 53 shows removal versus Duomac C concentration at pH 8.

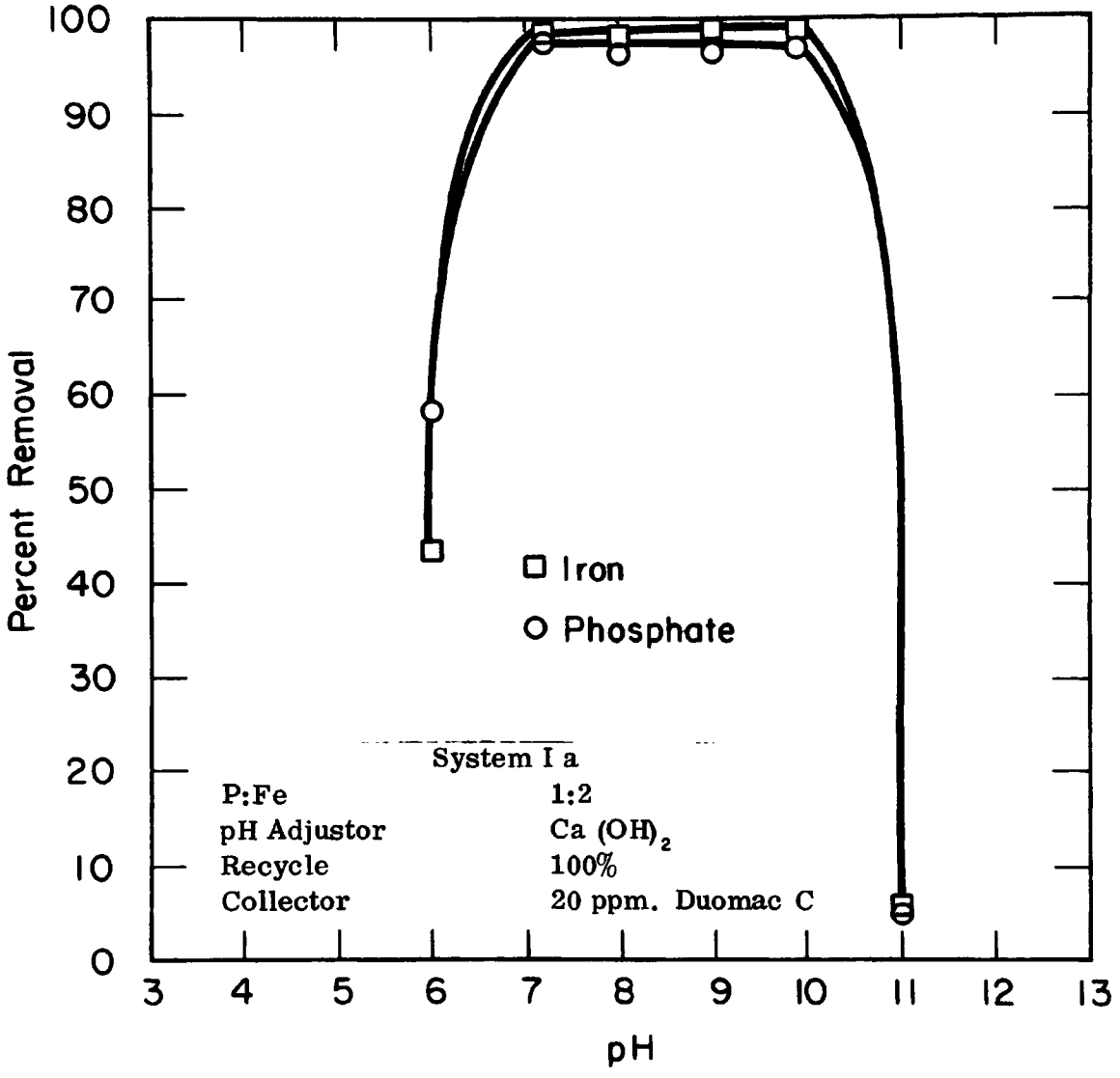


Figure 49. pH vs per cent removal.

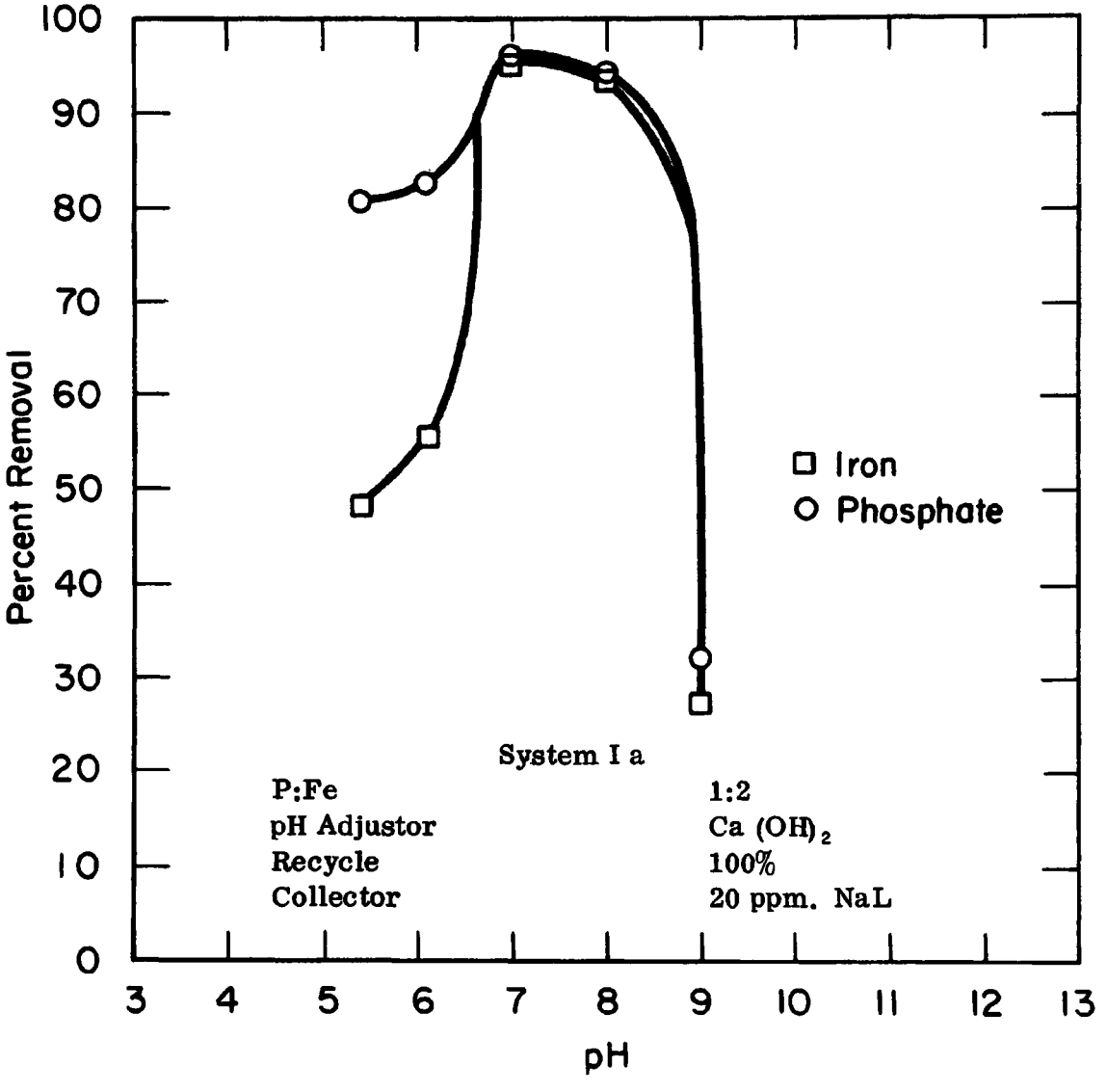


Figure 50. pH vs per cent removal.

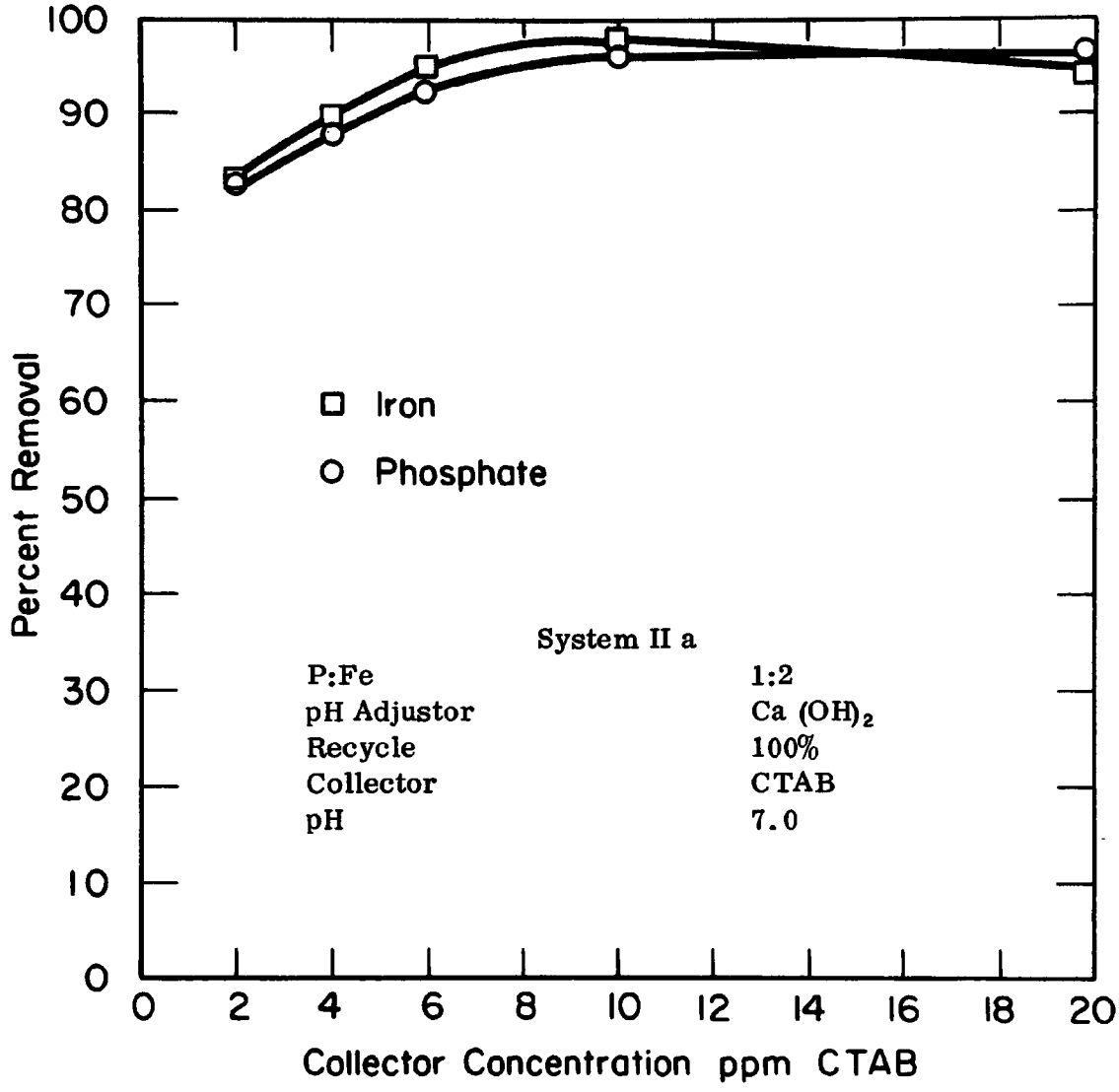


Figure 51. Collector concentration vs per cent removal.

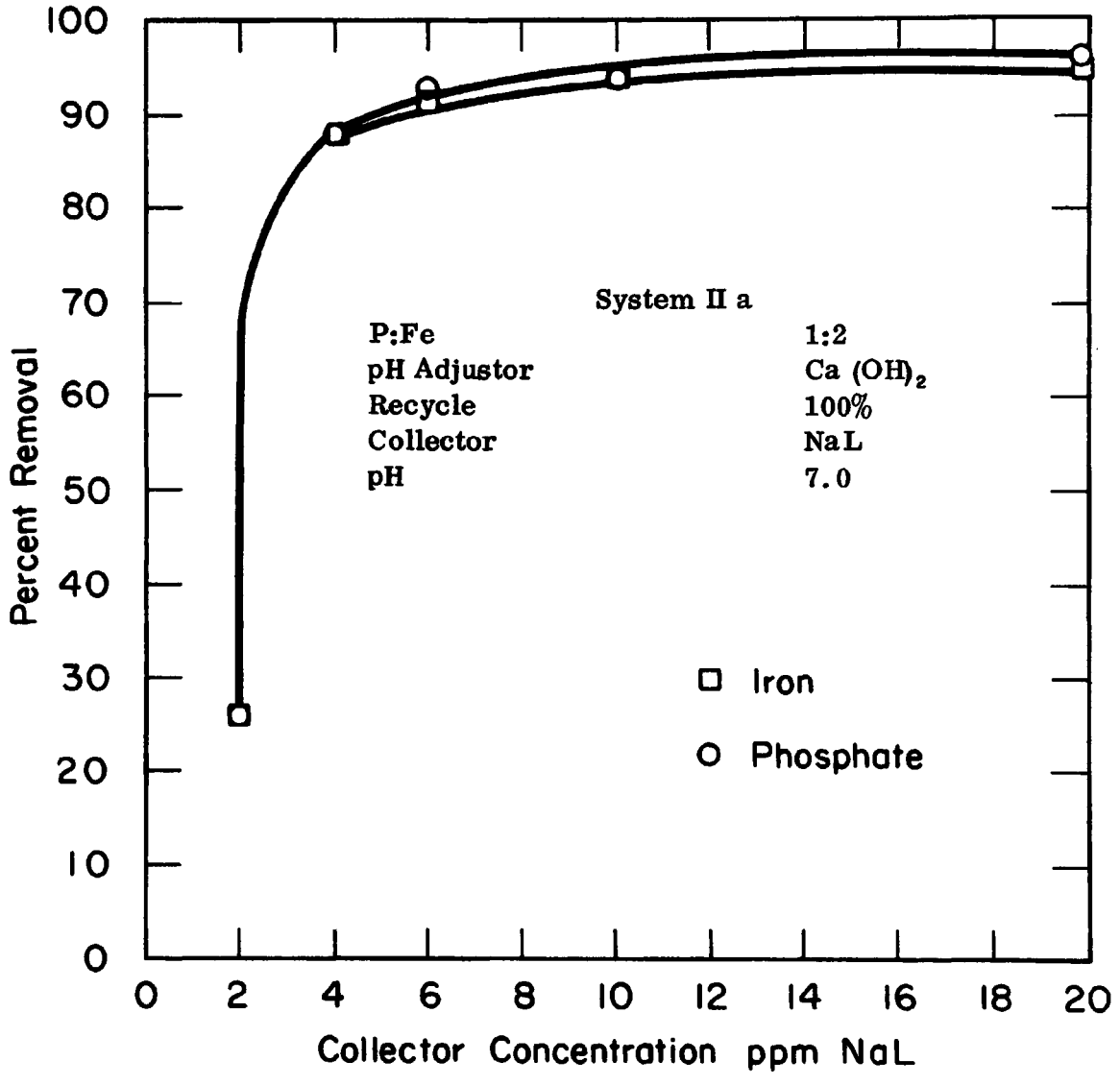


Figure 52. Collector concentration vs per cent removal.

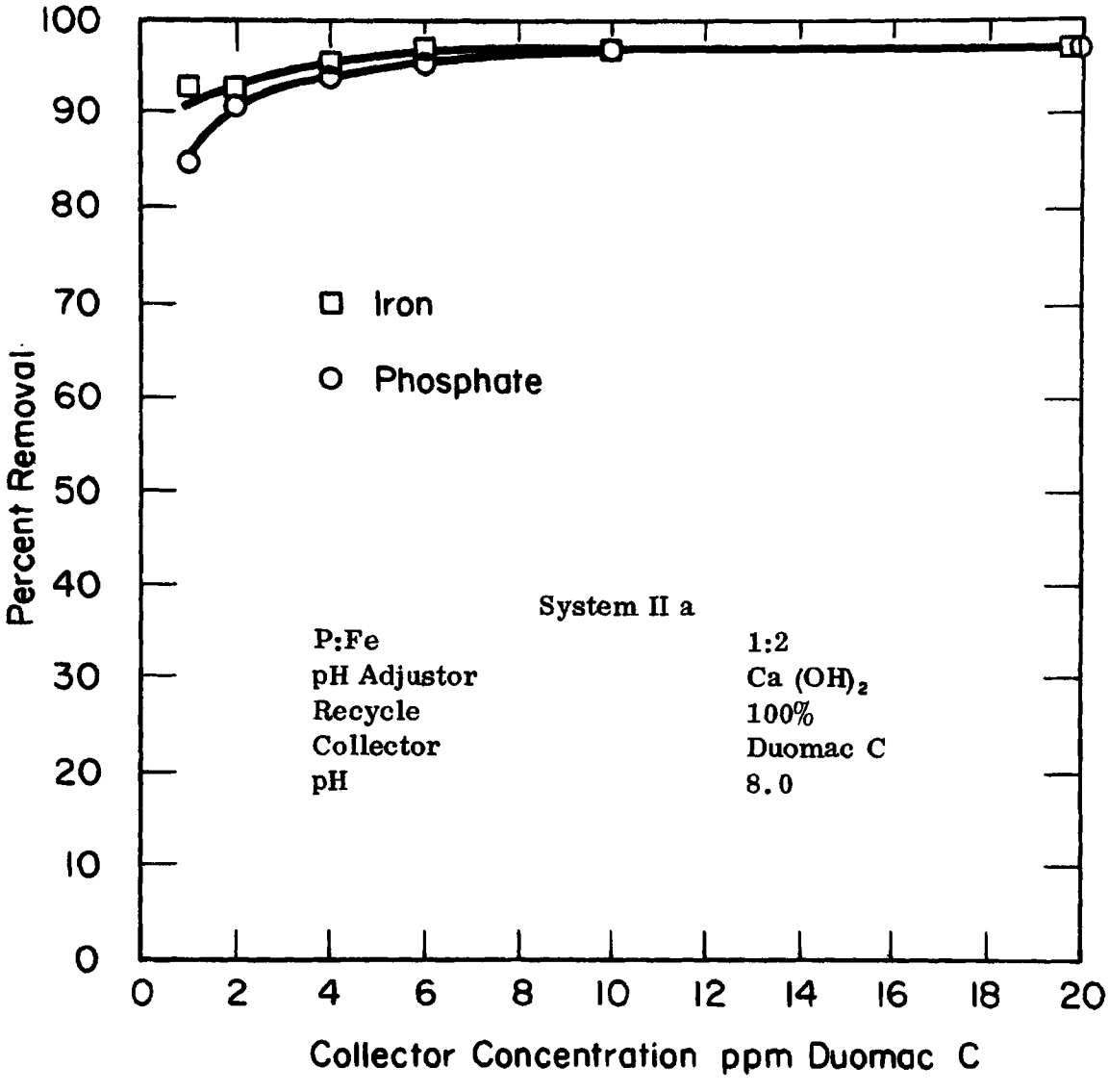


Figure 53. Collector concentration vs per cent removal.

(c) System IIIa

In this system, the major variable was the recycle ratio, and experimental runs were made using all three collector types. Quantitatively, the system components were:

KH_2PO_4	35 ppm as PO_4
$FeSO_4$	41.22 ppm as Fe(II)
$Ca(OH)_2$	as required for pH adjustment
Collector	10 ppm
Recycle Ratio	variable

Figure 54 shows iron and phosphate removal versus recycle ratio at pH 7 using 10 ppm Ctab, while Figures 55 and 56 are similar plots for 10 ppm NaL at pH 7.0 and for 10 ppm Duomac C at pH 8.0 respectively.

(d) System IVa

In this system the major variable is the P:Fe molar ratio, and experimental runs were made using all three collector types. Quantitatively, the system components were:

KH_2PO_4	35 ppm as PO_4
$FeSO_4$	variable
$Ca(OH)_2$	as required for pH adjustment
Collector	10 ppm

Figure 57 shows a plot of removal versus P:Fe molar ratio, using 10 ppm Ctab at pH 7.0, while Figures 58 and 59 show similar plots for 10 ppm NaL at pH 7.0 and for 10 ppm Duomac C at pH 8.0, respectively.

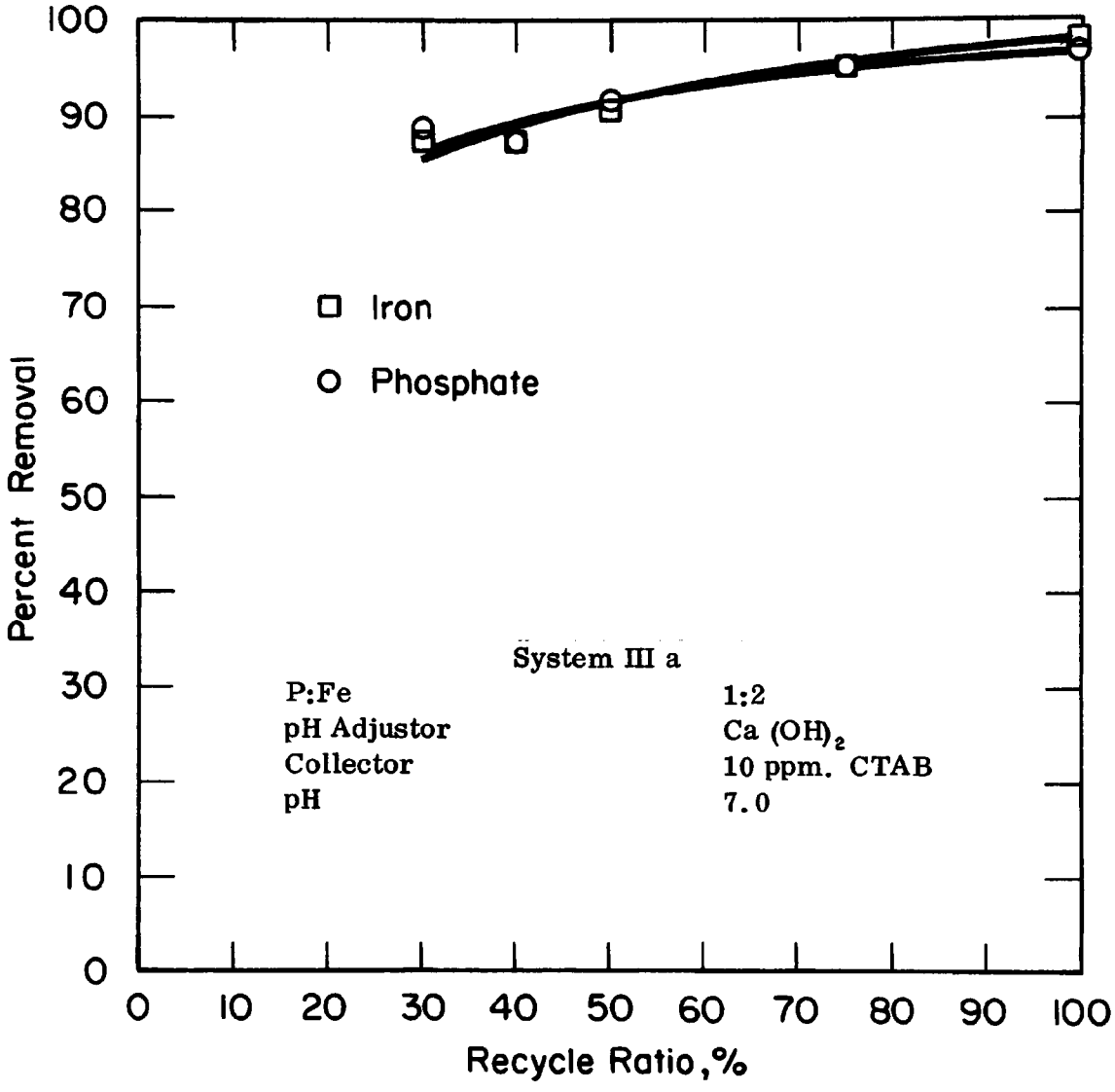


Figure 54. Recycle ratio vs per cent removal.

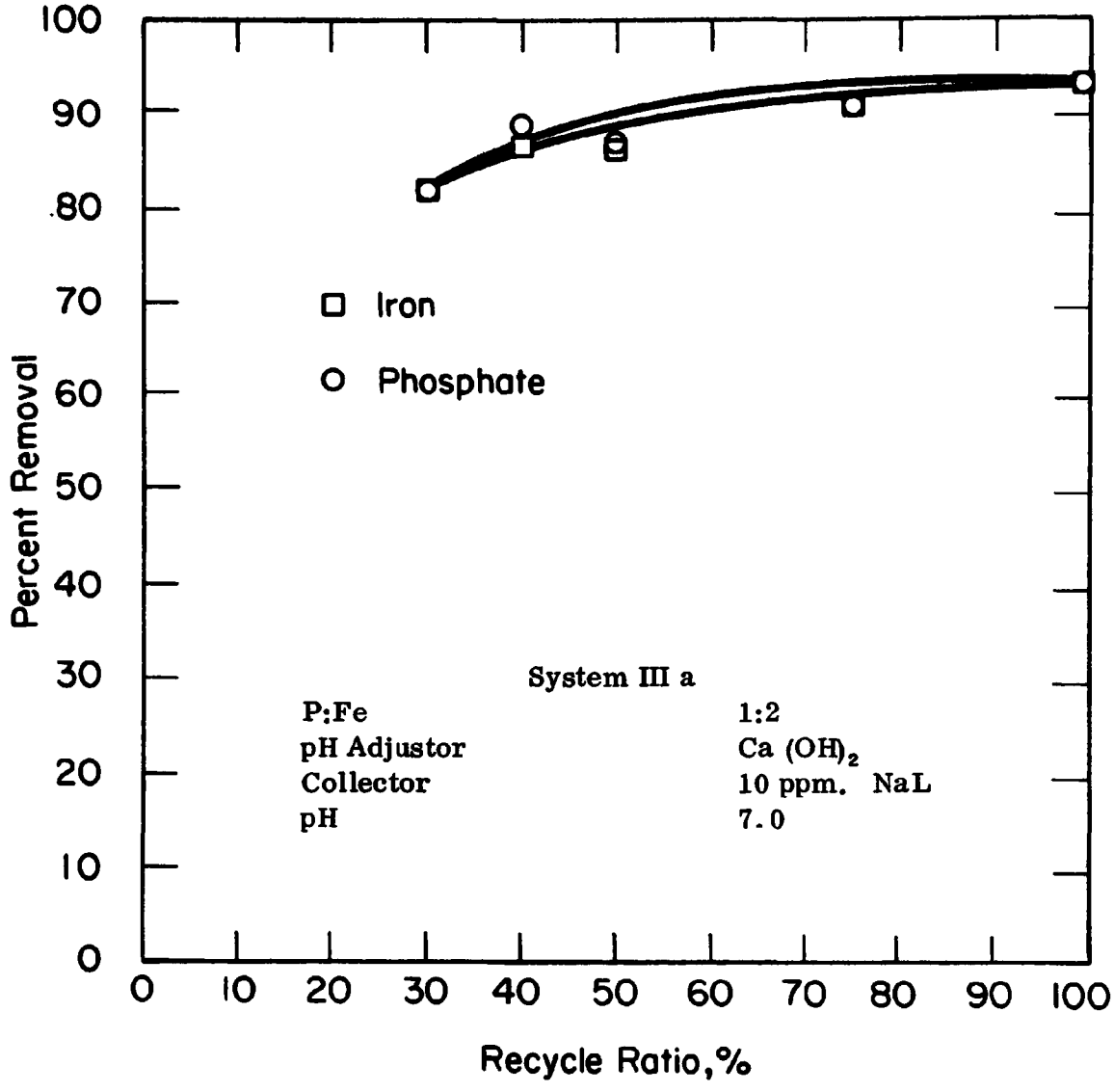


Figure 55. Recycle ratio vs per cent removal.

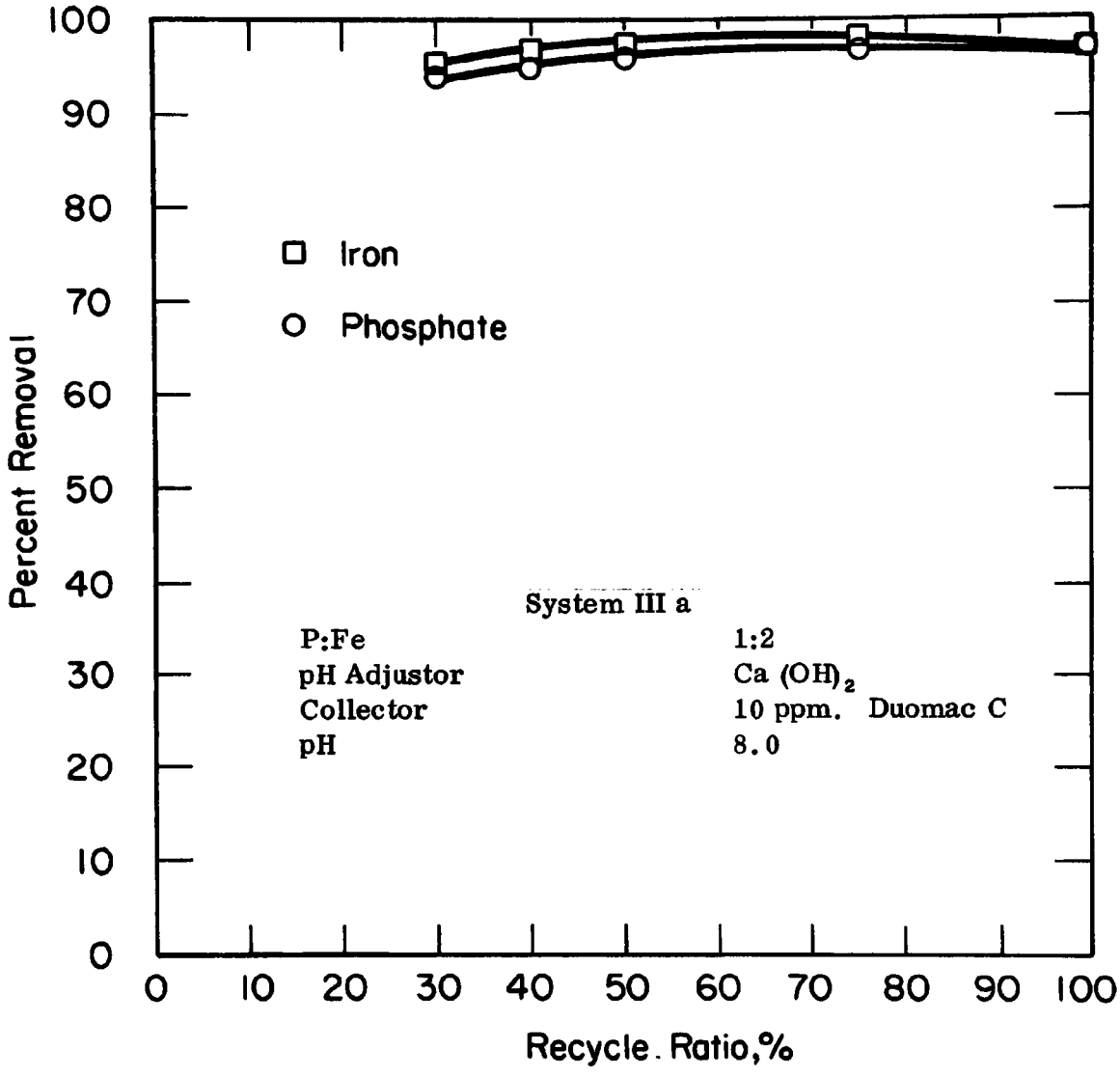


Figure 56. Recycle ratio vs per cent removal.

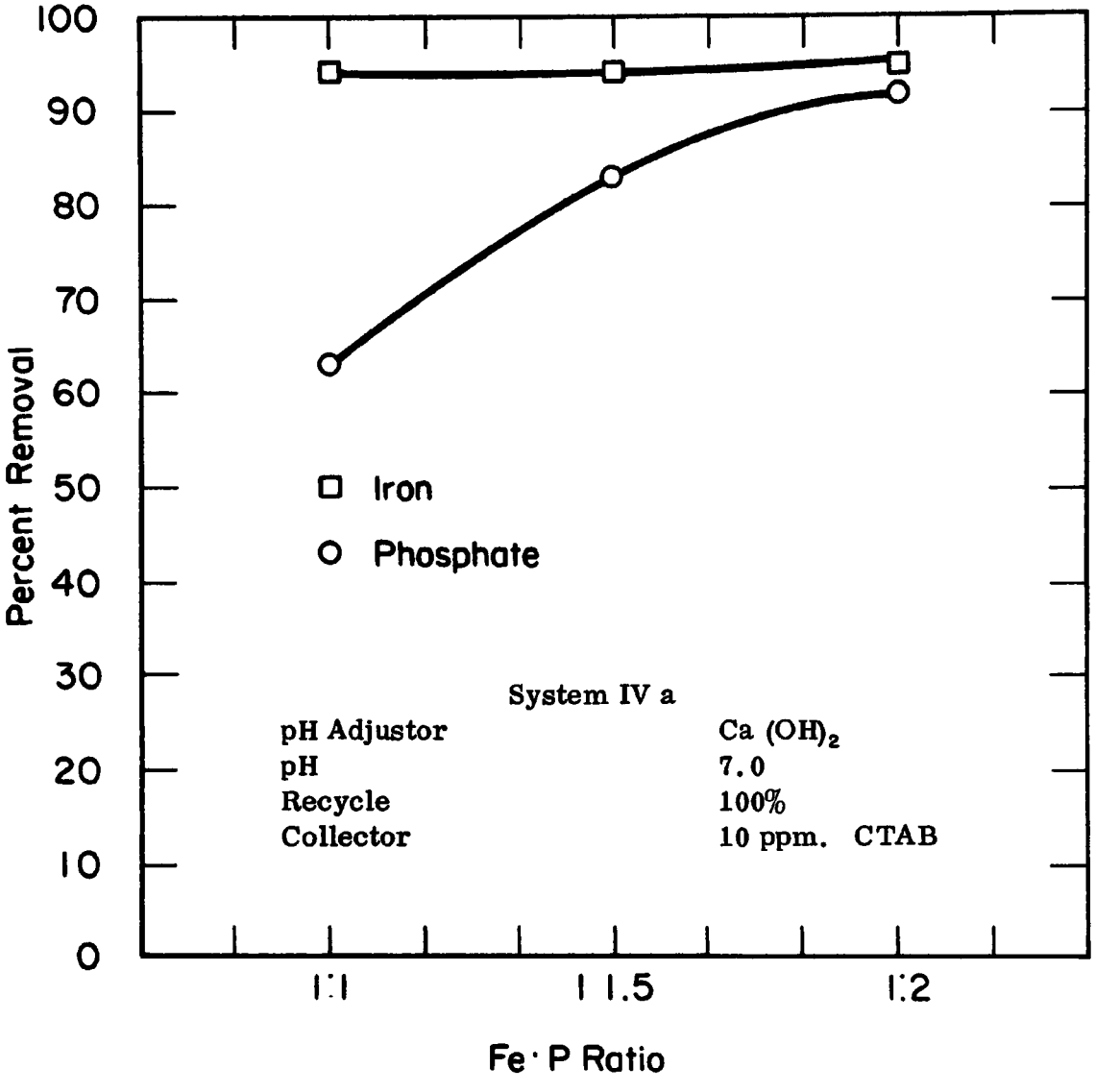


Figure 57. Fe:P ratio vs per cent removal.

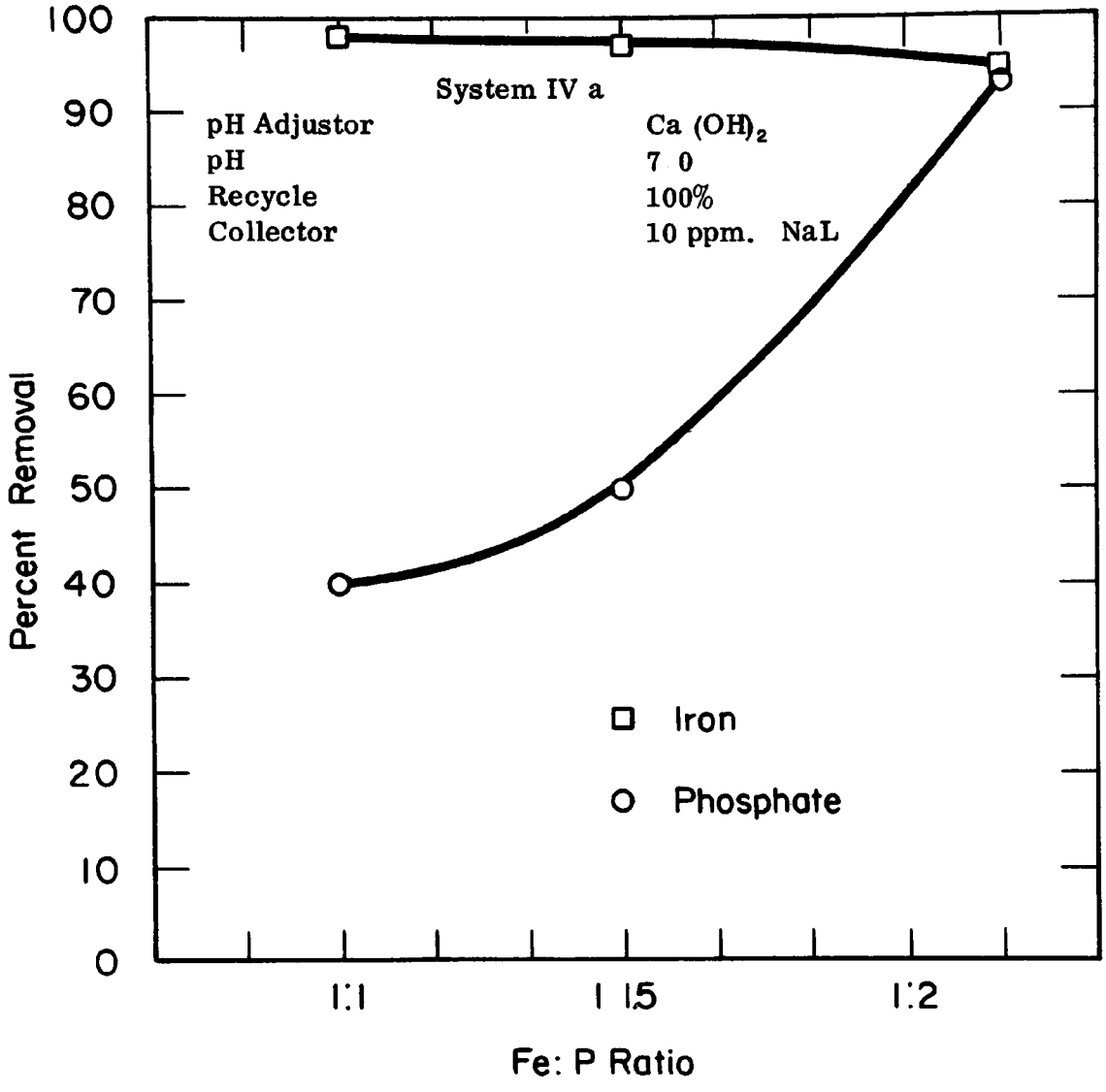


Figure 58. Fe:P ratio vs per cent removal.

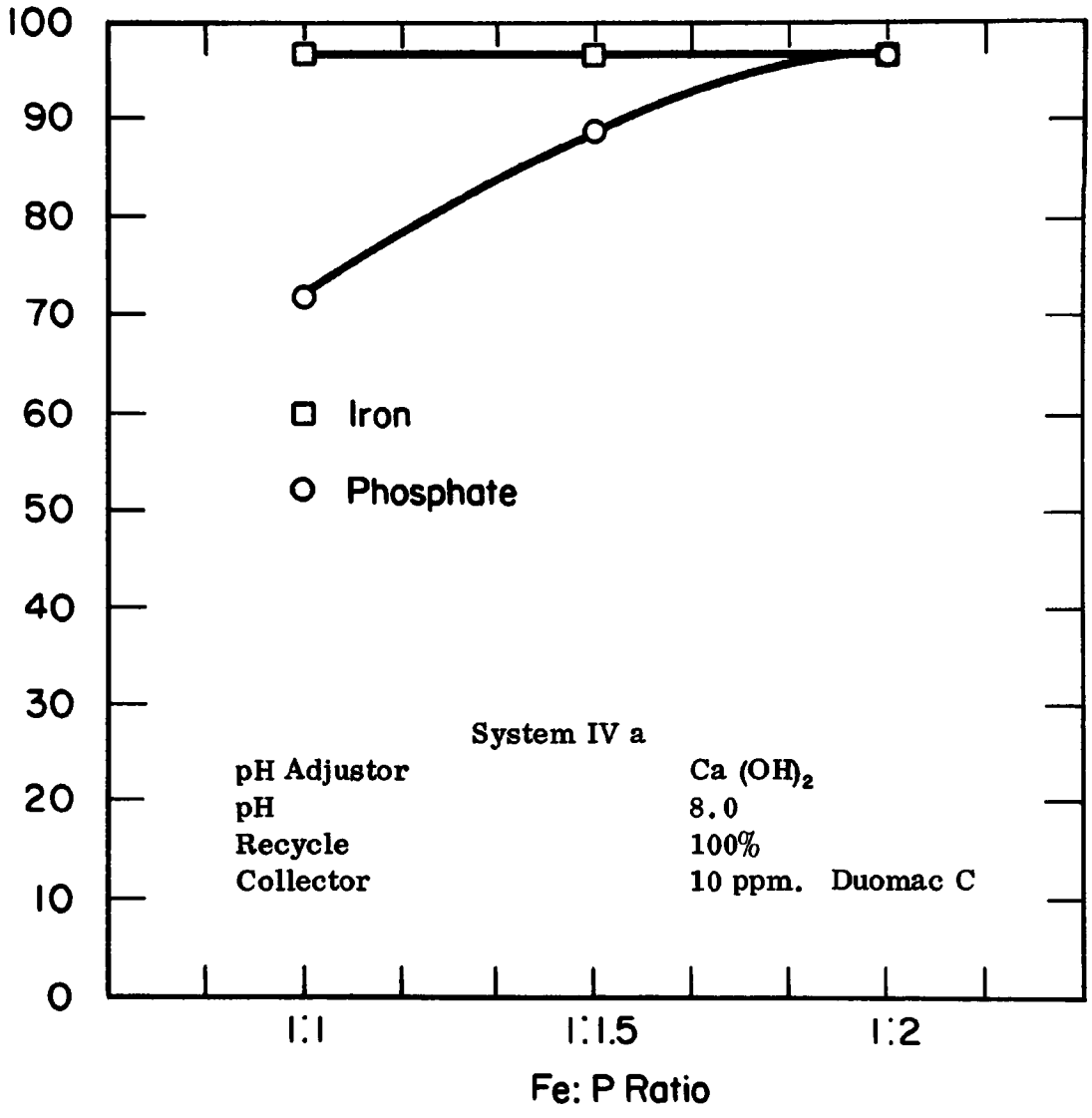


Figure 59. Fe:P ratio vs per cent removal.

(e) Air Requirements

One of the objectives of this work was to compare the efficiency of dissolved-air flotation with the efficiency of the microflotation system described in the previous subsection. The most suitable parameter for comparison is the air-to-solids ratio. For both systems, the weight of influent solids was calculated by assuming that all the phosphate was precipitated as $FePO_4$. The excess iron was assumed to form $Fe(OH)_3$. In both studies the phosphate and iron concentrations were the same, 35 ppm PO_4^{-3} and 41.22 ppm Fe.

In the dissolved-air flotation system, the amount of air released from solution upon reduction to atmospheric pressure was calculated from Henry's Law as 44.8 cm^3/liter at standard conditions and 100 percent recycle. For the microflotation system, 5 minutes of a 10 cm^3/min flow rate normally gave maximum removal. (See Figure 29). Thus, the air used amounted to 100 cm^3 at standard conditions over the five minute time period. From these figures an air-to-solids ratio more than twice as great is needed with microflotation to achieve nearly the same results as dissolved-air-flotation. Fifty percent recycle in the dissolved-air flotation gave good phosphate and iron removals with an air-to-solids ratio of 0.313, less than one-fourth that required by microflotation.

With microflotation a great deal of a frothing agent such as ethyl alcohol is required for production of very small bubbles. On a large sewage plant scale, the addition of a frothing agent would not only add to the operating cost but also increase the amount of organics in the effluent stream. It would not be necessary for a plant using dissolved air-flotation to cope with these problems since with this system a frothing agent is not necessary for production of very small bubbles.

During the current investigation it was observed that the sludge volume resulting from dissolved-air flotation is much less than that produced by sedimentation. On a plant scale this factor would reduce the size of the equipment necessary to handle the sludge.

Conclusions

System I

(1) Ninety-eight percent phosphate removal can be obtained by dissolved-air flotation with 20 ppm Duomac C in the pH range 7.0 to 10.0.

(2) Ninety-five percent phosphate removal is possible by dissolved-air flotation with 20 ppm NaL in the pH range 7.0 to 8.0.

System II

(1) The optimum surfactant concentration forCtab, NaL and Duomac C is approximately 10 ppm at the optimum pH values of 7.0, 7.0 and 8.0 respectively.

(2) Collector concentrations above 10 ppm did not improve the phosphate removal. This result is attributed to the formation of a complete adsorption monolayer of surfactant at 10 ppm concentration.

(3) The phosphate removal showed a direct proportionality to surfactant concentration below 10 ppm Ctab.

System III

(1) In the case of all three surfactants, the highest phosphate removal occurred at a recycle ratio of 100 percent.

(2) The removal of phosphate by flotation with Duomac C was highly resistant to variances in the recycle ratio. At 30 percent recycle, over 90 percent phosphate removal can be achieved by dissolved-air flotation with 10 ppm Duomac C at a pH of 8.0.

System IV

(1) The optimum Fe:P molar ratio is 2:1 in the case of each surfactant. The maximum iron and phosphate removals were obtained at this point.

(2) With Fe:P molar ratios less than 2:1 the removal of iron is near its maximum but the removal of phosphate drops severely as the ratio is lowered.

(3) Competition for iron between hydroxide and phosphate ions causes the low phosphate removals below a Fe:P ratio of 2:1.

General

(1) Flotation with Duomac C proved to be the best overall system. High phosphate removals can be achieved at low surfactant concentrations and at low recycle ratios.

(2) Much less sludge volume is formed in dissolved-air flotation than in sedimentation.

(3) Flotation of phosphate precipitates is possible without the use of a frothing agent. Dissolved air flotation without a frothing agent is just as effective as microflotation, which requires a frothing agent.

SECTION 8

REMOVAL OF PHOSPHATE FROM WASTEWATER WITH FERROUS SULFATE

The purpose of the work described below was as follows:

(1) To evaluate the total phosphate removal with ferrous sulfate from a municipal wastewater treatment plant secondary effluent.

(2) To observe the effect of substances usually present in secondary effluent on the phosphate removal.

(3) To compare the results of phosphate removal from secondary effluent with results obtained from runs using pure phosphate solution under similar conditions.

(4) To explore the possible application of ferrous sulfate to remove phosphate concurrently with simulated activated sludge process.

All work was done on a laboratory bench scale and batch processes were used. The secondary and primary effluent samples were taken from Grove City, Ohio, Sewage Treatment Plant.

Experimental Procedure

Samples of secondary effluent were collected in two one gallon polyethelene bottles and delivered to the laboratory. Samples for determination of total phosphate and COD were taken from one bottle while the other was kept under refrigeration. As soon as the total phosphate was determined (approximately 3 hours) the quantities of $FeSO_4 \cdot 7H_2O$ were calculated, to arrive at the specified mole ratio of Fe to P, and weighed. 800 ml samples from the other water sample bottle were transferred to 1000 ml beakers, the oxygen content and the

pH were measured, $FeSO_4 \cdot 7H_2O$ was added and dissolved and the pH was adjusted with 0.2 normal $Ca(OH)_2$ suspension while stirring at 100 RPM for 5 minutes. The stirring speed was then reduced to 20 RPM and continued for 20 more minutes then the solids were allowed to settle at quiescent conditions for specified periods of time. When polyelectrolites were used to aid the coagulation and flocculation they were added at the end of the rapid mix period. Total phosphate, iron, and COD were determined in the supernatant solution.

The primary effluent samples were taken at the outlet of the primary settling tank and samples from the activated sludge process were taken from the aeration tank at a point approximately one fifth of the tank length from the inlet of the primary effluent. The samples were immediately delivered to the laboratory. The filtered primary effluent was analyzed for total phosphates and COD. Two 800 ml portions of the activated sludge process samples were transferred to 1000 ml beakers and reactivated by passing dispersed air through the samples at such a flow rate that the oxygen concentration was maintained at 2 to 3 mg/l. The samples were also stirred at 40 RPM during the aeration. Using the results of total phosphate determination in the primary effluent the quantity of $FeSO_4 \cdot 7H_2O$ to be added was estimated on the basis of 800 ml primary effluent. After two hours of reactivation the activated sludge process samples were allowed to settle at quiescent conditions (approximately 5 minutes) and 520 ml of the supernatant (65 percent) were syphoned off and replaced with 520 ml primary effluent. To one of the samples was added the estimated quantity of $FeSO_4 \cdot 7H_2O$ and the other was run as a control. The suspensions were stirred at 40 RPM,

and dispersed air was passed through the suspensions to maintain an oxygen concentration between 2 to 3 mg/l. After the specified aeration time the solids were allowed to settle for one hour. The supernatant solutions were analyzed for total phosphates, iron and COD.

The equipment and the procedure for dissolved air flotation are described in Section 7. The only difference here was that instead of pure phosphate solution 500 ml samples of secondary effluent were used. The total phosphate of the secondary effluent was determined and ferrous sulfate was added in quantities to attain the specified iron to phosphorus mole ratio.

The total phosphates were determined as follows:

To 100.0 ml of the sample solution in 250 ml conical flask were added 0.5 ml H_2SO_4-conc. and 8 g of potassium persulfate. The use of potassium persulfate was suggested by D. E. Sanning (22). The solution was gently boiled for 90 minutes, maintaining the total volume between 20 and 40 ml (if necessary distilled water was added). The solution was allowed to cool and transferred to 100 ml volumetric flask and diluted to the mark. A 25.0 ml aliquot (or less) was transferred to another 100 ml volumetric flask and the determination was completed using the hydrazine-molybdenum blue colorimetric method described in Section 5, omitting the addition of perchloric acid.

COD was determined by the method described in Standard Methods for examination of Water and Wastewater, Twelfth Edition, 1965, pp. 510-514.

The equipment and measuring devises are described in Section 6.

RESULTS AND DISCUSSION

Removal of Phosphate From Secondary Effluent and Separation of Solids by Sedimentation

The variation of total phosphate concentration in Grove City Sewage Treatment Plant secondary effluent was caused primarily by the rain water entering the sewage drainage system. The total phosphate in the samples varied from 3.5 to 14.2 mg/l. Other properties of the secondary effluent were as follows:

pH = from 7.3 to 7.6

dissolved oxygen from 3.8 to 4.4 mg/l

and COD from 8.6 to 23.0 mg/l.

Table VII shows the results arranged in decreasing order of initial total phosphate concentration. The phosphate removal is primarily determined by the Fe:P mole ratio. 46.0 to 88.5 percent phosphate was achieved at Fe:P = 1.0, the residual phosphate concentration was from 1.32 to 2.10 mg/l P. 75.3 to 96.4 Percent total phosphate was removed at Fe:P = 2.0, residual phosphate concentrations was 0.18 to 0.45 mg/l P. The results show that to attain residual phosphate concentration of less than 0.8 mg/l P the quantity of $FeSO_4 \cdot 7\ H_2O$ added should correspond to at least a mole ratio of iron to phosphorus of 1.5.

Table VII also shows that the percent phosphate removal decreases with decreasing initial total phosphate concentration. The residual phosphate concentration is associated with dissolved oxygen concentration in the secondary effluent and the quantity of $FeSO_4 \cdot 7H_2O$

TABLE VII. PHOSPHATE REMOVAL WITH $FeSO_4 \cdot 7H_2O$ FROM GROVE CITY SEWAGE TREATMENT PLANT SECONDARY EFFLUENT

Run No.	Secondary Effluent: Initial Total Phosphate mg/l P	Secondary Effluent: Added $FeSO_4 \cdot 7H_2O$ to mole ratio Fe:P	Supernatant: Settling time hours	Supernatant: pH	Supernatant: Phosphate mg/l P	Supernatant: Iron mg/l	Phosphate Removal Percent
1	14.15	1.0	1	8.6	1.62	0.60	88.5
2	14.15	1.5	1	8.6	0.53	0.72	96.2
3	14.15	2.0	1	8.6	0.45	1.12	96.8
4	11.0	1.0	1	8.6	1.58	0.44	85.6
5	11.0	1.5	1	8.6	0.39	0.40	96.4
6	11.0	2.0	1	8.6	0.23	0.92	97.9
7	9.0	1.0	1	7.5	2.00	1.40	77.7
8	9.0	1.5	1	7.5	0.47	2.04	94.7
9	9.0	2.0	1	7.5	0.25	2.36	97.2
10	9.0	1.0	1	8.0	2.10	1.50	76.6
11	9.0	1.5	1	8.1	0.35	1.42	96.1
12	9.0	2.0	1	8.0	0.28	1.86	96.8
13	9.0	1.0	4	7.5	1.32	1.06	85.3
14	9.0	1.5	4	7.5	0.45	1.74	95.0
15	9.0	2.0	4	7.5	0.26	2.08	97.1
16	9.0	1.0	4	8.0	1.98	1.18	78.0
17	9.0	1.5	4	8.1	0.45	1.16	95.0
18	9.0	2.0	4	8.0	0.26	1.48	97.1
19	7.54	1.0	1	8.1	1.36	0.43	82.0
20	7.54	1.5	1	8.0	0.50	0.82	93.4
21	7.54	2.0	1	8.0	0.18	1.34	97.6
22	4.84	1.0	1	8.0	1.50	1.00	68.3
23	4.84	1.5	1	8.0	0.43	1.32	91.1
24	4.84	2.0	1	8.0	0.25	1.92	94.8
25	3.48	1.0	1	8.0	1.88	1.08	46.0
26	3.48	1.5	1	8.0	0.86	1.48	75.3
27	3.48	2.0	1	8.0	0.40	1.90	88.5
28	3.48	1.0	4	8.0	1.80	1.10	48.0
29	3.48	1.5	4	8.0	0.85	1.40	75.6
30	3.48	2.0	4	8.0	0.40	1.74	88.5
			Added 1 mg/l C-7				
31	7.54	1.0	1	8.0	1.44	0.27	80.9
32	7.54	1.5	1	8.0	0.38	0.45	95.0
33	7.54	2.0	1	8.1	0.14	0.52	98.0
			Added 1 mg/l A-23				
34	4.84	1.0	1	8.0	1.56	1.56	67.8
35	4.84	1.5	1	8.0	0.89	2.12	81.6
36	4.84	2.0	1	8.0	0.40	2.60	91.7

added. Let us consider the results of residual concentration of phosphate in the supernatant of 0.45, 0.23, 0.25, 0.18, 0.25 and 0.40 mg/l P respectively. The average dissolved oxygen concentration in the secondary effluent at the time of ferrous sulfate addition was close to 4.2 mg/l. Simple calculations show that there was a deficiency of dissolved oxygen for complete oxygenation of ferrous iron in samples used for runs 3, 6, and 9 (-3.1, -1.5, and -0.4 mg/l O_2 respectively). The oxygen concentration in run 21 was very close to the theoretical amount required for complete oxygenationcof ferrous iron and the residual concentration of phosphate was the minimum (0.18 mg/l P). The oxygen concentration in runs 24 and 27 was in excess (+1.7 and +2.4 mg/l iron. The results follow the pattern predicted by the assumed mechanism discussed in Section 6.

Comparison of runs 7 through 9, 10 through 12, 13 through 15, and 16 through 18 shows that the phosphate removal is not affected by the pH in the range of 7.5 to 8.0.

The phosphate removal was only slightly affected by settling time from 1 to 4 hours (see runs 7 through 9, 13 through 15, 10 through 12, 16 through 18, 25 through 28, and 28 through 30).

The runs 31 through 33 show the results obtained by addition of 1 mg/l cationic polyelectrolyte C-7 manufactured by Rohm and Haas. The runs 34 through 36 show the results of addition of 1 mg/l Purifloc A-23 a high molecular weight anionic polyelectrolyte manufactured by the Dow Chemical Company. Comparing runs 31 through 33 to runs 19 through 21 and runs 34 through 36 to runs 22 through 24 no significant difference is observed. It should be mentioned that the conditions at which the polyelectrolytes were used probably were not the most favorable.

The residual concentration of iron in the supernatant varied from 0.40 to 2.36 mg/l (runs 1 through 30, Table VII). The relatively high residual concentration of iron was attributed to the solubility of ferrous hydroxide which was present in solutions containing less dissolved oxygen than required for complete oxygenation of ferrous iron, and slow coagulation and flocculation of the ferric hydroxide formed. The residual ferric iron in the supernatant was reduced by approximately 50 percent by addition of C-7 as shown by the results of runs 31 through 33 when compared to runs 19 through 21.

On addition of $FeSO_4 \cdot 7H_2O$ to the secondary effluent the pH of the solution decreased by 0.2 to 0.4 pH units depending on the quantity of $FeSO_4 \cdot 7H_2O$ added. The relatively small decrease of pH, compared to runs made with pure phosphate solutions, was due to the buffering capacity of the secondary effluent. The quantities of $Ca(OH)_2$ suspension required to raise the pH to the specified value were from 20 to 60 mg/l CaO depending on the quantity of $FeSO_4 \cdot 7H_2O$ added and were relatively high compared to runs with pure phosphate solutions. Again, the effect of the buffering capacity of secondary effluent is apparent. The coagulation, flocculation and sedimentation of the formed precipitates (runs 1 through 30) was fast and the supernatant was clear after one hour settling time. The addition of polyelectrolytes increased the flocculation and settling rates during the initial settling period.

Up to 20 percent decrease of COD was observed when sufficient dissolved oxygen was present for complete oxygenation of ferrous iron. It is expected that the presence of ferrous iron in supernatant will increase the COD, a fact verified by the experimental results.

From a practical point of view the phosphate removal from secondary effluent with ferrous sulfate was the same when compared to phosphate removal from pure phosphate solutions at similar conditions and indicates that the contaminants commonly occurring in secondary effluent do not affect the phosphate removal.

Separation of the Insolubilized Phosphates by Dissolved Air Flotation Technique

The best results of phosphate removal by dissolved air flotation from pure phosphate solutions were achieved using Duomac C (N-CoCo-1,3 diamino propane acetate) manufactured by Armour Industrial Chemicals. Therefore Duomac C was used as collector in runs of phosphate removal from secondary effluent. The first series of experiments with secondary effluent showed that the froth stability was much lower compared to runs with pure phosphate solutions at similar conditions. At least 20 ppm of Duomac C were required (based on the volume of secondary effluent) to form a stable froth and clear separation of insolubilized phosphates. With 10 ppm of Duomac C the insolubilized phosphates (initial concentration of phosphates 11.0 mg/l P and Fe:P = 1.0 to 2.0) were carried to the surface but the froth collapsed and the solids re-entered the solution. The phosphate removal was 95 percent and did not show the expected variation with Fe:P ratio observed in runs with pure phosphate solutions. It is probable that at a high collector concentration, ion flotation also takes place together with flotation of precipitate. More work is required to resolve the many factors affecting the phosphate removal with ferrous sulfate from secondary effluent using dissolved air flotation technique.

Phosphate Removal With Ferrous Sulfate in a Simulated Activated Sludge Process

The main purpose of this exploratory work was to observe the effect of oxygenation rate on phosphate removal. It was speculated that the low concentration of oxygen (2 to 3 mg/l O_2) and the oxygen consumption in the activated sludge process will considerably lower the oxygenation rate of ferrous iron and therefore a higher phosphate removal may be expected. (See Discussion, Section 6). Run PE 7, Table VII, shows a residual concentration of total phosphate 0.40 mg/l P at Fe:P = 1.25. Based on the results shown in Table VIIIa higher residual phosphate concentration than 0.40 mg/l at Fe:P = 1.25 was expected and indicates that at mole ratio of Fe to P from 1.5 to 1.0 higher phosphate removal is attained in the activated sludge process compared to phosphate removal from secondary effluent.

Table VIII shows that 91 to 97 percent phosphate was removed in the simulated activated sludge process on addition of ferrous sulfate and only 14 to 22 percent phosphate removal was accomplished by the activated sludge process without addition of ferrous sulfate (control runs).

Table VIII shows that the residual concentration of iron (0.04 to 0.19 mg/l Fe) is much lower than results shown in Table VII (runs 1 through 30:0.44 to 2.4 mg/l Fe).

The pH of the solution (primary effluent plus activated sludge) decreased only by 0.1 to 0.3 units on addition of $FeSO_4 \cdot 7H_2O$ and did not change during the aeration process. No pH adjusting reagents were used in the runs shown in Table VIII.

TABLE VIII. PHOSPHATE REMOVAL WITH FERROUS SULFATE IN A SIMULATED ACTIVATED SLUDGE PROCESS

Run No.	Primary Effluent				Supernatant					Percent P removed
	pH	COD mg/l	P mg/l	Fe:P	Aeration time hours	pH	COD mg/l	P mg/l	Fe mg/l	
PE 1	7.6	68.0	7.62	2.0	2	7.3	14.0	0.71	0.19	90.7
Control	7.6	68.0	7.62	0	2	7.6	14.0	5.96	0.11	21.8
PE 4	7.4	140	9.52	1.5	3	7.3	23.0	0.30	0.13	96.8
Control	7.4	140	9.52	0	3	7.4	20.0	7.72	0.08	18.9
PE 7	7.2	75.2	7.66	1.25	4	7.1	10.1	0.40	0.04	94.8
Control	7.2	75.2	7.66	0	4	7.2	8.0	6.60	0.02	13.8

No adverse effects on the settling rate of the solids with addition of ferrous sulfate were observed when compared to the control runs.

Efficient phosphate removal was attained with ferrous sulfate (up to 97 percent) in the simulated activated sludge process, the residual concentration of iron was very low(0.1 mg/l Fe and less) and no pH adjustment was required. It should be mentioned that much less additional equipment would be required for phosphate removal using ferrous sulfate concurrently with the activated sludge process as compared to a tertiary process of phosphate removal from secondary effluent with ferrous sulfate.

Conclusions

A. For the removal of phosphate from secondary effluent with ferrous sulfate and separation of insolubilized solids by sedimentation:

(1) From 75.3 to 97.9 percent total phosphate was removed at mole ratio of iron to phosphorus from 1.5 to 2.0. The phosphate removal decreased rapidly below an iron to phosphorus mole ratio of 1.5. The percent phosphate removal decreased with decreasing initial phosphate concentration. Economic considerations suggest a mole ratio of iron to phosphorus of 1.5 to 2.0.

(2) Phosphate removal was not affected by the pH in range 7 to 8.

(3) Higher phosphate removal was attained at dissolved oxygen concentration just sufficient for complete oxygenation of ferrous iron.

(4) No adverse effect of organic matter present in the secondary effluents was observed on phosphate removal. The phosphate removal from secondary effluent was similar to phosphate removal from oxygen containing pure phosphate solutions at similar conditions.

(5) The residual concentration of iron in the supernatant was from 0.6 to 2.3 mg/l Fe and was similar to the iron left in the supernatant by phosphate removal from pure phosphate solutions at similar conditions.

B. For removal of insolubilized phosphates from secondary effluent by dissolved air flotation technique:

(1) Ninety-five percent phosphate removal from secondary effluent was achieved by dissolved air flotation using Duomac C (20 ppm) as collector, with 100 percent "reflux" and at pH = 8.0.

(2) The froth stability was lower compared to runs with pure phosphate solutions at the same conditions. The adsorption of organic compounds, present in the secondary effluent, on the solid particles formed apparently interferred with the adsorption of collector and affected the froth stability.

(3) Phosphate removal from secondary effluent did not show the pronounced effect of mole ratio of iron to phosphorus observed by separation of insolubilized phosphates from pure phosphate solutions using dissolved air flotation techniques.

(4) More work is required to determine the feasibility of dissolved air flotation technique for phosphate removal from secondary effluent.

C. For phosphate removal with ferrous sulfate in a simulated activated sludge process:

(1) Ninety-one to 97 percent total phosphate was removed in a simulated activated sludge process when ferrous sulfate was added. Only 14 to 22 percent phosphate was removed by the simulated activated sludge process when no ferrous sulfate was added.

(2) Higher phosphate removal was attained at an iron to phosphorous mole ratio from 1.0 to 1.5 compared to phosphate removal from secondary effluent by sedimentation at the same iron to phosphorus ratio.

(3) No addition of calcium hydroxide for pH adjustment was required to attain efficient phosphate removal with ferrous sulfate in a simulated activated sludge process. The pH decreased only by 0.1 to 0.2 units an addition of ferrous sulfate.

(4) The residual concentration of iron (0.04 to 0.19 mg/l Fe) in the supernatant solution was lower compared to the residual concentration of iron(0.44 to 2.3 mg/l Fe) in supernatant when removing phosphate with ferrous sulfate from secondary effluent by sedimentation.

(5) Exploratory studies showed that ferrous sulfate could be used as very efficient means for phosphate removal in an activated sludge process.

Acknowledgements

The invaluable advise, suggestions, and help given by Dr. Edwin E. Smith, Professor, Department of Chemical Engineering, The Ohio State University, and Dr. Kenesaw S. Shumate, Associate Professor, Department of Civil Engineering, The Ohio State University, during preparation of this report is deeply appreciated.

Valuable contributions were made by Chun-jen Wang, Scott M. Barrick, James F. Dietz and Jeffrey T. Kuo, all graduate students in the Department of Chemical Engineering who worked on the project.

To undergraduate students Paul D. Bartholf, Charles A. Klingensmith and Lewis Clark gratitude is expressed for help on routine work on the project.

The financial support of the Department of Interior Office of Water Resources Research, Allotment Project A-011-OHIO is gratefully acknowledged.

Addendum

Master's of Science Theses

Three Master's of Science theses as follows have derived up to date from this study:

(1) Wang, Chun-jen, "The Removal of Phosphate From Water With Ferrous Sulfate," master's thesis, The Ohio State University, (1968).

(2) Barrick, S. M., "The Precipitation and Flotation of Orthophosphate Using Ferrous Sulfate, Ferric Sulfate and Calcium Hydroxide," master's thesis, The Ohio State University, (1969).

(3) Dietz, J. F., "The Precipitation and Dissolved-Air Flotation of Orthophosphate Using Ferrous Sulfate and Calcium Hydroxide," Master's Thesis, The Ohio State University,(1969).

References

1. Sawyer, C. N., "Some New Aspects of Phosphates in Relation to Lane Fertilization," Sew. and Ind. Wastes, Vol. 24, No. 6, p. 768-776 (1962).

2. Lea, W. L., Rohlich, G. A., and Katz, W. T., "Removal of Phosphates From Treated Sewage", Sewage and Industrial Wastes, 26, 261 (1954).

3. Rippert, Irmgard, "Moglichkeiten zu Phosphat - Elimination aus Abwassern auf Chemischen Wege", Gesundh.-Ing. 79, 333 (1958).

4. Arne Henriksen, "Laboratory Studies on the Removal of Phosphates From Sewage by Coagulation Process, Schweiz. Z. Hydrol., 24, 253-271 (1962).

5. Ronald F. Wukasch, "The Dow Process for Phosphorus Removal" for the FWPCA Phosphorus Removal Symposium, Chicago, Illinois, June 1968. The Dow Chemical Company, Chemical Building, 2020 Abbott Road Center, Midland, Michigan 48640.

6. Schuster, G., "Grundlagen der Phosphatelimination durch chemische Fallung". Fortschr. Wasserchem. Ihrer Grenzgeb. (8) 188-203 (1968).

7. Rudolf, G., Uhlmann, D., "Fallmittelzugabe in Gawasser." Fortschr. Wasserchem. Ihrer Grenzgeb. (8) 268-278 (1968).

8. Van Vuuren, L. R., et al., "Advanced Purification of Sewage Works Effluent Using a Combined System of Lime Softening and Flotation", Water Research, Pergamon Press 1967, Vol. 1, pp. 463-474. Printed in Great Britian.

9. Chun-jen Wang, "The Removal of Phosphate From Water With Ferrous Sulfate", M.S. Thesis, Ohio State University, Chemical Engineering Department, 1968.

10. Caldwell, D. H. and Adams, R. B. "Colorimetric Determination of Iron in Water With O-Phenanthroline". Journal of American Water and Waste Association. 38:727 (1946).

11. Werner Stumm. "Oxygenation of Ferrous Iron". Water Pollution Control Research Series. DAST-28 14010 06/69.

12. Cher, M., and Davidson, N., "The Kinetics of the Oxygenation of Ferrous Iron in Phosphoric Acid Solutions", J. Amer. Chem. Soc., 77, 793 (1955).

13. King, T., and Davidson, N., "Kinetics of Ferrous Iron-Oxygen Reaction in Acid Phosphate-Pyrophosphate Solutions", J. Amer. Chem. Soc., 80, 1542 (1958).

14. Rubin, A. J., Cassel, A., and Johnson, J. D. "Microflotation: New Low Gas-Flow Rate Foam Separation Technique for Bacteria and Algae," Biotechnology and Bioengineering, Vol. III, 135 (1966).

15. Rubin, A. J., Cassel, A. "Removal of Organic Colloids by Microflotation," 23rd Purdue Industrial Waste Conference (May, 1968).

16. Rubin, A. J., Lackey, S. C. "Effect of Coagulation on the Microflotation of Bacillus cereus", Water Resources Center, The Ohio State University.

17. Rubin, A. J., "Microflotation: Coagulation and Foam Separation of Aerobacter Aerogenes," Biotechnology and Bioengineering, Vol. X, 89 (1968).

18. Rubin, A. J., "Removal of Trace Metals by Foam Separation Process", Journal of American Water Works Association, 60, 7 (July, 1968).

19. Rubin, A. J., Johnson, J. D., and Lamb III, J. C., "Comparison of Variables in Ion and Precipitate Flotation," Industrial and Engineering Chemistry Process Design and Development, Vol. 5, 368 (October, 1966).

20. Barrick, S. M. "The Precipitation and Flotation of Orthophosphate Using Ferrous Sulfate, Ferric Sulfate, andCalcium Hydroxide," Master's Thesis, The Ohio State University (1969).

21. Dietz, J. F. "The Precipitation and Dissolved Air Flotation of Orthophosphate Using Ferrous Sulfate and Calcium Hydroxide, Master's Thesis, The Ohio State University (1969).

22. Sanning, D. E., "Phosphorus Determination - A Method Evaluation", Water and Sewage Works, 114(4), 131-133 (1967).